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## (57) Abstract

The present invention relates to an improved filler material for use in forming metal matrix composites. Particularly, the filler has specific characteristics which enhance formation processes and/or improve the mechanical and/or physical properties of resultant metal matrix composite bodies.

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## DESCRIPTION

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FILLER MATERIAL FOR METAL MATRIX COMPOSITESTechnical Field

The present invention relates to an improved filler material for use in forming metal matrix composites. Particularly, the filler has specific characteristics which enhance formation processes and/or improve the mechanical and/or physical properties of resultant metal matrix composite bodies.

Background Art

Composite products comprising a metal matrix and a strengthening or reinforcing phase such as ceramic particulates, whiskers, fibers or the like, show great promise for a variety of applications because they combine some of the stiffness and wear resistance of the reinforcing phase with the ductility and toughness of the matrix metal. Generally, a metal matrix composite will show an improvement in such properties as strength, stiffness, contact wear resistance, coefficient of thermal expansion (C.T.E.), density, thermal conductivity and elevated temperature strength retention relative to the matrix metal in monolithic form, but the degree to which any given property may be improved depends largely on the specific constituents, their volume or weight fraction, and how they are processed in forming the composite. In some instances, the composite also may be lighter in weight than the matrix metal per se. Aluminum matrix composites reinforced with ceramics such as silicon carbide in particulate, platelet, or whisker form, for example, are of interest because of their higher specific stiffness (e.g., elastic modulus over density), wear resistance, thermal conductivity, low coefficient of thermal expansion (C.T.E.) and high temperature strength and/or specific strength (e.g., strength over density) relative to aluminum.

Various metallurgical processes have been described for the fabrication of aluminum matrix composites, including methods based on powder metallurgy techniques and liquid-metal infiltration techniques which make use of pressure casting, vacuum casting, stirring, and wetting agents. With powder metallurgy techniques, the metal in the form of a powder and the reinforcing material in

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the form of a powder, whiskers, chopped fibers, etc., are admixed and then either cold-pressed and sintered, or hot-pressed. The maximum ceramic volume fraction in silicon carbide reinforced aluminum matrix composites produced by this method has been reported to be about 25 volume percent in the case of whiskers, and about 40 volume percent in the case of particulates.

The production of metal matrix composites by powder metallurgy techniques utilizing conventional processes imposes certain limitations with respect to the characteristics of the products attainable. The volume fraction of the ceramic phase in the composite is limited typically, in the case of particulates, to about 40 percent. Also, the pressing operation poses a limit on the practical size attainable. Only relatively simple product shapes are possible without subsequent processing (e.g., forming or machining) or without resorting to complex presses. Also, nonuniform shrinkage during sintering can occur, as well as nonuniformity of microstructure due to segregation in the compacts and grain growth.

U.S. Patent No. 3,970,136, granted July 20, 1976, to J. C. Cannell et al., describes a process for forming a metal matrix composite incorporating a fibrous reinforcement, e.g. silicon carbide or alumina whiskers, having a predetermined pattern of fiber orientation. The composite is made by placing parallel mats or felts of coplanar fibers in a mold with a reservoir of molten matrix metal, e.g., aluminum, between at least some of the mats, and applying pressure to force molten metal to penetrate the mats and surround the oriented fibers. Molten metal may be poured onto the stack of mats while being forced under pressure to flow between the mats. Loadings of up to about 50% by volume of reinforcing fibers in the composite have been reported.

The above-described infiltration process, in view of its dependence on outside pressure to force the molten matrix metal through the stack of fibrous mats, is subject to the vagaries of pressure-induced flow processes, i.e., possible non-uniformity of matrix formation, porosity, etc. Non-uniformity of properties is possible even though molten metal may be introduced at a multiplicity of sites within the fibrous array. Consequently, complicated mat/reservoir arrays and flow pathways need to be provided to achieve adequate and uniform penetration of the stack of fiber mats. Also, the aforesaid pressure-infiltration method allows for only a relatively low reinforcement to matrix volume fraction to be achieved because of the difficulty inherent in infiltrating a large mat volume. Still further, molds are required to contain



the molten metal under pressure, which adds to the expense of the process. Finally, the aforesaid process, limited to infiltrating aligned particles or fibers, is not directed to formation of aluminum metal matrix composites reinforced with materials in the form of randomly oriented particles, whiskers  
5 or fibers.

In the fabrication of aluminum matrix-alumina filled composites, aluminum does not readily wet alumina, thereby making it difficult to form a coherent product. Various solutions to this problem have been suggested. One such approach is to coat the alumina with a metal (e.g., nickel or tungsten),  
10 which is then hot-pressed along with the aluminum. In another technique, the aluminum is alloyed with lithium, and the alumina may be coated with silica. However, these composites exhibit variations in properties, or the coatings can degrade the filler, or the matrix contains lithium which can affect the matrix properties.

15 U.S. Patent No. 4,232,091 to R. W. Grimshaw et al., overcomes certain difficulties in the art which are encountered in the production of aluminum matrix-alumina composites. This patent describes applying pressures of 75-375 kg/cm<sup>2</sup> to force molten aluminum (or molten aluminum alloy) into a fibrous or whisker mat of alumina which has been preheated to 700 to 1050°C. The maximum  
20 volume ratio of alumina to metal in the resulting solid casting was 0.25/1. Because of its dependency on outside force to accomplish infiltration, this process is subject to many of the same deficiencies as that of Cannell et al.

European Patent Application Publication No. 115,742 describes making aluminum-alumina composites, especially useful as electrolytic cell  
25 components, by filling the voids of a preformed alumina matrix with molten aluminum. The application emphasizes the non-wettability of alumina by aluminum, and therefore various techniques are employed to wet the alumina throughout the preform. For example, the alumina is coated with a wetting agent of a diboride of titanium, zirconium, hafnium, or niobium, or with a  
30 metal, i.e., lithium, magnesium, calcium, titanium, chromium, iron, cobalt, nickel, zirconium, or hafnium. Inert atmospheres, such as argon, are employed to facilitate wetting. This reference also shows applying pressure to cause molten aluminum to penetrate an uncoated matrix. In this aspect, infiltration is accomplished by evacuating the pores and then applying pressure to the  
35 molten aluminum in an inert atmosphere, e.g., argon. Alternatively, the preform can be infiltrated by vapor-phase aluminum deposition to wet the

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surface prior to filling the voids by infiltration with molten aluminum. To assure retention of the aluminum in the pores of the preform, heat treatment, e.g., at 1400 to 1800°C, in either a vacuum or in argon is required. Otherwise, either exposure of the pressure infiltrated material to gas or  
5 removal of the infiltration pressure will cause loss of aluminum from the body.

The use of wetting agents to effect infiltration of an alumina component in an electrolytic cell with molten metal is also shown in European Patent Application Publication No. 0094353. This publication describes production of  
10 aluminum by electrowinning with a cell having a cathodic current feeder as a cell liner or substrate. In order to protect this substrate from molten cryolite, a thin coating of a mixture of a wetting agent and solubility suppressor is applied to the alumina substrate prior to start-up of the cell or while immersed in the molten aluminum produced by the electrolytic process.  
15 Wetting agents disclosed are titanium, zirconium, hafnium, silicon, magnesium, vanadium, chromium, niobium, or calcium, and titanium is stated as the preferred agent. Compounds of boron, carbon and nitrogen are described as being useful in suppressing the solubility of the wetting agents in molten aluminum. The reference, however, does not suggest the production of metal  
20 matrix composites, nor does it suggest the formation of such a composite in, for example, a nitrogen atmosphere.

In addition to application of pressure and wetting agents, it has been disclosed that an applied vacuum will aid the penetration of molten aluminum into a porous ceramic compact. For example, U.S. Patent No. 3,718,441,  
25 granted February 27, 1973, to R. L. Landingham, reports infiltration of a ceramic compact (e.g., boron carbide, alumina and beryllia) with either molten aluminum, beryllium, magnesium, titanium, vanadium, nickel or chromium under a vacuum of less than  $10^{-6}$  torr. A vacuum of  $10^{-2}$  to  $10^{-6}$  torr resulted in poor wetting of the ceramic by the molten metal to the extent that the metal did  
30 not flow freely into the ceramic void spaces. However, wetting was said to have improved when the vacuum was reduced to less than  $10^{-6}$  torr.

U.S. Patent No. 3,864,154, granted February 4, 1975, to G. E. Gazza et al., also shows the use of vacuum to achieve infiltration. This patent describes loading a cold-pressed compact of  $AlB_{12}$  powder onto a bed of cold-pressed aluminum powder. Additional aluminum was then positioned on top of  
35 the  $AlB_{12}$  powder compact. The crucible, loaded with the  $AlB_{12}$  compact

"sandwiched" between the layers of aluminum powder, was placed in a vacuum furnace. The furnace was evacuated to approximately  $10^{-5}$  torr to permit outgassing. The temperature was subsequently raised to  $1100^{\circ}\text{C}$  and maintained for a period of 3 hours. At these conditions, the molten aluminum penetrated the porous  $\text{AlB}_{12}$  compact.

U.S. Patent No. 3,364,976, granted January 23, 1968 to John N. Reding et al., discloses the concept of creating a self-generated vacuum in a body to enhance penetration of a molten metal into the body. Specifically, it is disclosed that a body, e.g., a graphite mold, a steel mold, or a porous refractory material, is entirely submerged in a molten metal. In the case of a mold, the mold cavity, which is filled with a gas reactive with the metal, communicates with the externally located molten metal through at least one orifice in the mold. When the mold is immersed into the melt, filling of the cavity occurs as the self-generated vacuum is produced from the reaction between the gas in the cavity and the molten metal. Particularly, the vacuum is a result of the formation of a solid oxidized form of the metal. Thus, Reding et al. disclose that it is essential to induce a reaction between gas in the cavity and the molten metal. However, utilizing a mold to create a vacuum may be undesirable because of the inherent limitations associated with use of a mold. Molds must first be machined into a particular shape; then finished, machined to produce an acceptable casting surface on the mold; then assembled prior to their use; then disassembled after their use to remove the cast piece therefrom; and thereafter reclaim the mold, which most likely would include refinishing surfaces of the mold or discarding the mold if it is no longer acceptable for use. Machining of a mold into a complex shape can be very costly and time-consuming. Moreover, removal of a formed piece from a complex-shaped mold can also be difficult (i.e., cast pieces having a complex shape could be broken when removed from the mold). Still further, while there is a suggestion that a porous refractory material can be immersed directly in a molten metal without the need for a mold, the refractory material would have to be an integral piece because there is no provision for infiltrating a loose or separated porous material absent the use of a container mold (i.e., it is generally believed that the particulate material would typically disassociate or float apart when placed in a molten metal). Still further, if it was desired to infiltrate a particulate material or loosely formed preform, precautions should be taken so that the infiltrating metal does not displace

at least portions of the particulate or preform resulting in a non-homogeneous microstructure.

The production of metal matrix composite bodies which include relatively fine reinforcement materials (e.g., small diameter particles) can be even more difficult to achieve relative to larger diameter particles. Accordingly, the formation of metal matrix composite bodies utilizing relatively fine reinforcement materials provides even greater difficulties.

The present invention ameliorates many of the difficulties encountered by the prior art by providing a filler material which can be utilized with a number of metal matrix composite formation processes, including a spontaneous infiltration process, which results in very desirable metal matrix composite bodies. Moreover, the incorporation of, for example, fine filler materials into a matrix metal can result in enhanced mechanical and/or physical properties of formed composite bodies.

#### Discussion of Commonly-Owned Patents and Patent Applications

The subject matter of this application is related to that of several other copending and commonly owned patent applications and issued Patents. Particularly, these other copending and commonly owned patent applications and issued Patents describe novel methods for making metal matrix composite materials (hereinafter sometimes referred to as "Commonly Owned Metal Matrix Patents and Patent Applications").

A novel method of making a metal matrix composite material is disclosed in Commonly Owned U.S. Patent No. 4,828,008, which issued May 9, 1989, from U.S. Patent Application Serial No. 049,171, filed May 13, 1987, in the names of White et al., and entitled "Metal Matrix Composites" which published in the EPO on November 17, 1988, as Publication No. 0291441. According to the method of this White et al. invention, a metal matrix composite is produced by infiltrating a permeable mass of filler material (e.g., a ceramic or a ceramic-coated material) with molten aluminum containing at least about 1 percent by weight magnesium, and preferably at least about 3 percent by weight magnesium. Infiltration occurs spontaneously without the application of external pressure or vacuum. A supply of the molten metal alloy is contacted with the mass of filler material at a temperature of at least about 675°C in the presence of a gas comprising from about 10 to 100 percent, and preferably at least about 50 percent, nitrogen by volume, and a remainder of the gas, if

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any, being a nonoxidizing gas, e.g., argon. Under these conditions, the molten aluminum alloy infiltrates the ceramic mass under normal atmospheric pressures to form an aluminum (or aluminum alloy) matrix composite. When the desired amount of filler material has been infiltrated with the molten  
5 aluminum alloy, the temperature is lowered to solidify the alloy, thereby forming a solid metal matrix structure that embeds the reinforcing filler material. Usually, and preferably, the supply of molten alloy delivered will be sufficient to permit the infiltration to proceed essentially to the boundaries of the mass of filler material. The amount of filler material in  
10 the aluminum matrix composites produced according to the White et al. invention may be exceedingly high. In this respect, filler to alloy volumetric ratios of greater than 1:1 may be achieved.

Under the process conditions in the aforesaid White et al. invention, aluminum nitride can form as a discontinuous phase dispersed throughout the  
15 aluminum matrix. The amount of nitride in the aluminum matrix may vary depending on such factors as temperature, alloy composition, gas composition and filler material. Thus, by controlling one or more such factors in the system, it is possible to tailor certain properties of the composite. For some end use applications, however, it may be desirable that the composite contain  
20 little or substantially no aluminum nitride.

It has been observed that higher temperatures favor infiltration but render the process more conducive to nitride formation. The White et al. invention allows the choice of a balance between infiltration kinetics and nitride formation.

25 An example of suitable barrier means for use with metal matrix composite formation is described in Commonly Owned U.S. Patent No. 4,935,055, which issued on June 19, 1990, from U.S. Patent Application Serial No. 141,642, filed January 7, 1988, in the names of Michael K. Aghajanian et al., and entitled "Method of Making Metal Matrix Composite with the Use of a Barrier",  
30 which published in the EPO on July 12, 1989, as Publication No. 0323945. According to the method of this Aghajanian et al. invention, a barrier means (e.g., particulate titanium diboride or a graphite material such as a flexible graphite foil product sold by Union Carbide under the trade name GRAFOIL®) is disposed on a defined surface boundary of a filler material and matrix alloy  
35 infiltrates up to the boundary defined by the barrier means. The barrier means is used to inhibit, prevent, or terminate infiltration of the molten

alloy, thereby providing net, or near net, shapes in the resultant metal matrix composite. Accordingly, the formed metal matrix composite bodies have an outer shape which substantially corresponds to the inner shape of the barrier means.

5       The method of U.S. Patent No. 4,828,008 was improved upon by Commonly Owned and Copending U.S. Patent Application Serial No. 517,541, filed on April 24, 1990, which was a continuation of U.S. Patent Application Serial No. 168,284, filed March 15, 1988 (and now abandoned), in the names of Michael K. Aghajanian and Marc S. Newkirk and entitled "Metal Matrix Composites and  
10   Techniques for Making the Same", and which published in the EPO on September 20, 1989, as Publication No. 0333629. In accordance with the methods disclosed in these U.S. Patent Applications, a matrix metal alloy is present as a first source of metal and as a reservoir of matrix metal alloy which communicates with the first source of molten metal due to, for example,  
15   gravity flow. Particularly, under the conditions described in this patent application, the first source of molten matrix alloy begins to infiltrate the mass of filler material under normal atmospheric pressures and thus begins the formation of a metal matrix composite. The first source of molten matrix metal alloy is consumed during its infiltration into the mass of filler material  
20   and, if desired, can be replenished, preferably by a continuous means, from the reservoir of molten matrix metal as the spontaneous infiltration continues. When a desired amount of permeable filler has been spontaneously infiltrated by the molten matrix alloy, the temperature is lowered to solidify the alloy, thereby forming a solid metal matrix structure that embeds the  
25   reinforcing filler material. It should be understood that the use of a reservoir of metal is simply one embodiment of the invention described in this patent application and it is not necessary to combine the reservoir embodiment with each of the alternate embodiments of the invention disclosed therein, some of which could also be beneficial to use in combination with the present  
30   invention.

35       The reservoir of metal can be present in an amount such that it provides for a sufficient amount of metal to infiltrate the permeable mass of filler material to a predetermined extent. Alternatively, an optional barrier means can contact the permeable mass of filler on at least one side thereof to define a surface boundary.

Moreover, while the supply of molten matrix alloy delivered should be at least sufficient to permit spontaneous infiltration to proceed essentially to the boundaries (e.g., barriers) of the permeable mass of filler material, the amount of alloy present in the reservoir could exceed such sufficient amount so that not only will there be a sufficient amount of alloy for complete infiltration, but excess molten metal alloy could remain and be attached to the metal matrix composite body. Thus, when excess molten alloy is present, the resulting body will be a complex composite body (e.g., a macrocomposite), wherein an infiltrated ceramic body having a metal matrix therein will be directly bonded to excess metal remaining in the reservoir.

Further improvements in metal matrix technology can be found in commonly owned and copending U.S. Patent Application Serial No. 521,043, filed May 9, 1990, which was a continuation-in-part of U.S. Patent Application Serial No. 484,753, filed February 23, 1990, which was a continuation-in-part of U.S. Patent Application Serial No. 432,661, which was filed on November 7, 1989 (and now abandoned), which was a continuation-in-part of U.S. Patent Application Serial No. 416,327, filed October 6, 1989 (and now abandoned), which was a continuation-in-part application of U.S. Patent Application Serial No. 349,590, filed May 9, 1989 (and now abandoned), which in turn was a continuation-in-part application of U.S. Patent Application Serial No. 269,311, filed November 10, 1988 (and now abandoned), all of which were filed in the names of Michael K. Aghajanian et al. and all of which are entitled "A Method of Forming Metal Matrix Composite Bodies By A Spontaneous Infiltration Process, and Products Produced Therefrom" (an EPO application corresponding to U.S. Patent Application Serial No. 416,327 was published in the EPO on June 27, 1990, as Publication No. 0375588). According to these Aghajanian et al. applications, spontaneous infiltration of a matrix metal into a permeable mass of filler material or preform is achieved by use of an infiltration enhancer and/or an infiltration enhancer precursor and/or an infiltrating atmosphere which are in communication with the filler material or preform, at least at some point during the process, which permits molten matrix metal to spontaneously infiltrate the filler material or preform. Aghajanian et al. disclose a number of matrix metal/infiltration enhancer precursor/infiltrating atmosphere systems which exhibit spontaneous infiltration. Specifically, Aghajanian et al. disclose that spontaneous infiltration behavior has been observed in the aluminum/magnesium/nitrogen system; the

aluminum/strontium/nitrogen system; the aluminum/zinc/oxygen system; and the aluminum/calcium/nitrogen system. However, it is clear from the disclosure set forth in the Aghajanian et al. applications that the spontaneous infiltration behavior should occur in other matrix metal/infiltration enhancer precursor/infiltrating atmosphere systems.

Another related copending and commonly owned patent application is U.S. Patent Application Serial No. 07/672,064, filed March 18, 1991, which is a continuation-in-part of U.S. Patent Application Serial No. 07/269,308, filed November 10, 1988, which matured to U.S. Patent No. 5,000,247, and which issued on March 19, 1991, and naming as sole inventor John Thomas Burke and entitled "Method For Forming Metal Matrix Composite Bodies With A Dispersion Casting Technique and Products Produced Thereby" (an EPO application corresponding to U.S. Patent Application Serial No. 07/269,308 was published in the EPO on May 16, 1990, as EPO Publication No. 0 368 788). These patent applications relate to a novel method for forming metal matrix composite bodies. A permeable mass of filler material is spontaneously infiltrated by a molten matrix metal. Particularly, an infiltration enhancer and/or an infiltration enhancer precursor and/or an infiltrating atmosphere are in communication with the filler material, at least at some point during the process, which permits molten matrix metal to spontaneously infiltrate the filler material. After infiltration has been completed to a desired extent, additional matrix metal is added to that matrix metal which has spontaneously infiltrated the filler material to result in a suspension of filler material and matrix metal having a lower volume fraction of filler relative to matrix metal. The matrix metal then can be permitted to cool in situ or the mixture of matrix metal and filler material can be poured into a second container as a casting process to form a desired shape which corresponds to the second container. However, the formed suspension, whether cast immediately after being formed or after cooling and thereafter heating and casting, can be poured into a desired shape while retaining beneficial characteristics associated with spontaneously infiltrated metal matrix composites.

Each of the above-discussed Commonly Owned Metal Matrix Patents and Patent Applications describes methods for the production of metal matrix composite bodies and novel metal matrix composite bodies which are produced therefrom. The entire disclosures of all of the foregoing Commonly Owned Metal



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Matrix Patents and Patent Applications are expressly incorporated herein by reference.

#### Summary of the Invention

5           Use of the filler material of the present invention may enhance both the processing techniques used to manufacture metal matrix composite bodies, as well as improve the resultant mechanical and/or physical properties of metal matrix composite bodies which are produced with the novel filler (i.e., reinforcement material).

10           It is well known that a substantial effort has been placed on identifying suitable filler materials and/or combinations of filler materials for use as reinforcement(s) in various metal matrix composite bodies. The present invention provides a solution to a number of difficulties experienced by many metal matrix composite manufacturers. Specifically, filler materials  
15           containing one or more of the following features may provide for enhanced production (e.g, shorter processing times, lower processing temperatures, the reduced need (or no need) for wetting agents, simpler and/or more economical manufacturing apparatuses or assemblies, etc.) capabilities never before achievable. For example, morphology, aspect ratio, amount and size of flaws  
20           or defects, surface characteristics (e.g., surface roughness, surface area, etc.), size distribution of filler, coefficient of thermal expansion, etc., may individually, or collectively, contribute to enhanced processing and/or enhanced composite properties. For example, the synergism which may be  
25           achieved between a particular morphology, aspect ratio and surface characteristics of a filler material may provide for shorter processing times as well as enhanced or improved mechanical properties relative to a similar filler material (e.g., similar chemical composition and/or similar particle sizes) which does not have precisely the same combination of properties.

30           A particulate filler material which exhibits many of the above-discussed advantageous properties is shown in Figure 6 herein. This particulate filler is desirable because it is relatively fine in size (e.g., about 500 grit, that is an average particle diameter of about 17 microns), thus permitting desirable mechanical properties to be achieved in a metal matrix composite body. The filler also exhibits a morphology which includes a substantial  
35           lacking or substantial elimination of any high angle or sharp edges (e.g., most particles exhibit substantially rounded edges); the filler has an aspect

ratio closer to "1" than many other filler materials previously known; the filler contains a minimized number of surface flaws and an attempt has been made to reduce the critical flaw size within each particle of filler; the surface of the filler exhibits a microroughness which results in increased surface area on each of the filler particles relative to other fillers which have a smoother surface; and the filler has a desirable particle size distribution which enhances packing efficiency.

The filler material of the present invention can be utilized to enhance virtually any metal matrix composite production process including pressure casting, stirring of a filler into a matrix metal, squeeze casting and in a preferred embodiment of the invention, spontaneous infiltration.

Moreover, the filler material exhibits desirable flow characteristics in a dry form. Accordingly, the filler material may be, for example, poured into a mold of any desirable shape prior to being infiltrated to result in a relatively high volume percent of filler or reinforcement in a formed metal matrix composite body. The flowability of the filler in a dry form enhances the ability to form metal matrix composite bodies having complex shapes. The morphology, aspect ratio and/or size distribution of the filler are all important considerations for flowability of a filler in a dry state. The ability of a filler to flow enhances the ability of the filler to be shaped into a preform by most conventional techniques (e.g., pressing, pouring, extruding, etc.).

#### Definitions

"Aluminum", as used herein, means and includes essentially pure metal (e.g., a relatively pure, commercially available unalloyed aluminum) or other grades of metal and metal alloys such as the commercially available metals having impurities and/or alloying constituents such as iron, silicon, copper, magnesium, manganese, chromium, nickel, titanium, zinc, etc., therein. An aluminum alloy for purposes of this definition is an alloy or intermetallic compound in which aluminum is the major constituent.

"Aspect Ratio", as used herein, means the ratio of the length to the width of a two-dimensional image or representation of a particle. For the particles of the present application, the particle length is the length of the longest straight line segment which can be drawn through the particle image. The particle width is the perpendicular distance between the narrowest set of

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parallel lines which can be drawn bounding the particle image, wherein each of said parallel lines is tangential to a particle surface, but neither of said lines passes into the two-dimensional image of the particle.

"Balance Non-Oxidizing Gas", as used herein, means that any gas present in addition to the primary gas comprising the infiltrating atmosphere, is either an inert gas or a reducing gas which is substantially non-reactive with the matrix metal under the process conditions. Any oxidizing gas which may be present as an impurity in the gas(es) used should be insufficient to oxidize the matrix metal to any substantial extent under the process conditions.

"Barrier" or "barrier means", as used herein, means any suitable means which interferes, inhibits, prevents or terminates the migration, movement, or the like, of molten matrix metal beyond a surface boundary of a permeable mass of filler material or preform, where such surface boundary is defined by said barrier means. Suitable barrier means may be any such material, compound, element, composition, or the like, which, under the process conditions, maintains some integrity and is not substantially volatile (i.e., the barrier material does not volatilize to such an extent that it is rendered non-functional as a barrier).

Further, suitable "barrier means" includes materials which are substantially non-wettable by the migrating molten matrix metal under the process conditions employed. A barrier of this type appears to exhibit substantially little or no affinity for the molten matrix metal, and movement beyond the defined surface boundary of the mass of filler material or preform is prevented or inhibited by the barrier means. The barrier reduces any final machining or grinding that may be required and defines at least a portion of the surface of the resulting metal matrix composite product. The barrier may in certain cases be permeable or porous, or rendered permeable by, for example, drilling holes or puncturing the barrier, to permit gas to contact the molten matrix metal, etc.

"Carcass" or "Carcass of Matrix Metal", as used herein, refers to any of the original body of matrix metal remaining which has not been consumed during formation of the metal matrix composite body, and typically, if allowed to cool, remains in at least partial contact with the metal matrix composite body which has been formed. It should be understood that the carcass may also include a second or foreign metal therein.

"Filler", as used herein, is intended to include either single constituents or mixtures of constituents which are substantially non-reactive with and/or of limited solubility in the matrix metal and may be single or multi-phase. Fillers may be provided in a wide variety of forms and sizes, such as powders, flakes, platelets, microspheres, whiskers, bubbles, fibers, particulates, fiber mats, chopped fibers, spheres, pellets, tubules, refractory cloths, etc., and may be either dense or porous. "Filler" may also include ceramic fillers, such as alumina or silicon carbide, as fibers, chopped fibers, particulates, whiskers, bubbles, spheres, fiber mats, or the like, mixtures thereof, and ceramic-coated fillers such as carbon fibers coated with alumina or silicon carbide to protect the carbon from attack, for example, by a molten aluminum matrix metal. Fillers may also include metals in any desired configuration.

"Hot-Topping", as used herein, refers to the placement of a substance on one end (the "topping" end) of an at least partially formed metal matrix composite which reacts exothermically with at least one of the matrix metal and/or filler material and/or with another material supplied to the topping end. This exothermic reaction should provide sufficient heat to maintain the matrix metal at the topping end in a molten state while the balance of the matrix metal in the composite cools to solidification temperature.

"Infiltrating Atmosphere", as used herein, means that atmosphere which is present which interacts with the matrix metal and/or preform (or filler material) and/or infiltration enhancer precursor and/or infiltration enhancer and permits or enhances spontaneous infiltration of the matrix metal.

"Infiltration Enhancer", as used herein, means a material which promotes or assists in the spontaneous infiltration of a matrix metal into a filler material or preform. An infiltration enhancer may be formed from, for example, (1) a reaction of an infiltration enhancer precursor with an infiltrating atmosphere to form a gaseous species and/or (2) a reaction product of the infiltration enhancer precursor and the infiltrating atmosphere and/or (3) a reaction product of the infiltration enhancer precursor and the filler material or preform. Moreover, the infiltration enhancer may be supplied directly to at least one of the preform, and/or matrix metal, and/or infiltrating atmosphere and function in a substantially similar manner to an infiltration enhancer which has formed as a reaction between an infiltration enhancer precursor and another species. Ultimately, at least during the

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spontaneous infiltration, the infiltration enhancer should be located in at least a portion of the filler material or preform to achieve spontaneous infiltration and the infiltration enhancer may be at least partially reducible by the matrix metal.

5        "Infiltration Enhancer Precursor" or "Precursor to the Infiltration Enhancer", as used herein, means a material which when used in combination with (1) the matrix metal, (2) the preform or filler material and/or (3) an infiltrating atmosphere forms an infiltration enhancer which induces or  
10        assists the matrix metal to spontaneously infiltrate the filler material or preform. Without wishing to be bound by any particular theory or explanation, it appears as though it may be necessary for the precursor to the infiltration enhancer to be capable of being positioned, located or transportable to a location which permits the infiltration enhancer precursor to interact with the infiltrating atmosphere and/or the preform or filler material and/or the  
15        matrix metal. For example, in some matrix metal/infiltration enhancer precursor/infiltrating atmosphere systems, it is desirable for the infiltration enhancer precursor to volatilize at, near, or in some cases, even somewhat above the temperature at which the matrix metal becomes molten. Such volatilization may lead to: (1) a reaction of the infiltration enhancer  
20        precursor with the infiltrating atmosphere to form a gaseous species which enhances wetting of the filler material or preform by the matrix metal; and/or (2) a reaction of the infiltration enhancer precursor with the infiltrating atmosphere to form a solid, liquid or gaseous infiltration enhancer in at least a portion of the filler material or preform which enhances wetting;  
25        and/or (3) a reaction of the infiltration enhancer precursor within the filler material or preform which forms a solid, liquid or gaseous infiltration enhancer in at least a portion of the filler material or preform which enhances wetting.

30        "Matrix Metal" or "Matrix Metal Alloy", as used herein, means that metal which is utilized to form a metal matrix composite body (e.g., before infiltration) and/or that metal which is intermingled with a filler material to form a metal matrix composite body (e.g., after infiltration). When a specified metal is mentioned as the matrix metal, it should be understood that such matrix metal includes that metal as an essentially pure metal, a  
35        commercially available metal having impurities and/or alloying constituents

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therein, an intermetallic compound or an alloy in which that metal is the major or predominant constituent.

"Matrix Metal/Infiltration Enhancer Precursor/Infiltrating Atmosphere System" or "Spontaneous System", as used herein, refers to that combination of materials which exhibit spontaneous infiltration into a preform or filler material. It should be understood that whenever a "/" appears between an exemplary matrix metal, infiltration enhancer precursor and infiltrating atmosphere that the "/" is used to designate a system or combination of materials which, when combined in a particular manner, exhibits spontaneous infiltration into a preform or filler material.

"Metal Matrix Composite" or "MMC", as used herein, means a material comprising a two- or three-dimensionally interconnected alloy or matrix metal which has embedded a preform or filler material. The matrix metal may include various alloying elements to provide specifically desired mechanical and physical properties in the resulting composite.

A Metal "Different" from the Matrix Metal means a metal which does not contain, as a primary constituent, the same metal as the matrix metal (e.g., if the primary constituent of the matrix metal is aluminum, the "different" metal could have a primary constituent of, for example, nickel).

"Nonreactive Vessel for Housing Matrix Metal" means any vessel which can house or contain a filler material (or preform) and/or molten matrix metal under the process conditions and not react with the matrix and/or the infiltrating atmosphere and/or infiltration enhancer precursor and/or a filler material or preform in a manner which would be significantly detrimental to the spontaneous infiltration mechanism. The nonreactive vessel may be disposable and removable after the spontaneous infiltration of the molten matrix metal has been completed.

"Preform" or "Permeable Preform", as used herein, means a porous mass of filler or filler material which is manufactured with at least one surface boundary which essentially defines a boundary for infiltrating matrix metal, such mass retaining sufficient shape integrity and green strength to provide dimensional fidelity prior to being infiltrated by the matrix metal. The mass should be sufficiently porous to accommodate spontaneous infiltration of the matrix metal thereinto. A preform typically comprises a bonded array or arrangement of filler, either homogeneous or heterogeneous, and may be comprised of any suitable material (e.g., ceramic and/or metal particulates,

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powders, fibers, whiskers, etc., and any combination thereof). A preform may exist either singularly or as an assemblage.

5        "Reservoir", as used herein, means a separate body of matrix metal positioned relative to a mass of filler or a preform so that, when the metal is molten, it may flow to replenish, or in some cases to initially provide and subsequently replenish, that portion, segment or source of matrix metal which is in contact with the filler or preform.

10       "Spontaneous Infiltration", as used herein, means the infiltration of matrix metal into the permeable mass of filler or preform occurs without requirement for the application of pressure or vacuum (whether externally applied or internally created).

15       "Thin Coating", "Thin Metal Matrix Composite", "Thin Preform", or "Thin Sheet", as used herein, refers to a relative dimensional characteristic of a particular body. A "thin" dimension may range in numerical values from a few  
20       mils (e.g., the diameter of a particle of filler material) to several inches or feet. In the case of a "thin" metal matrix composite plate or preform, "thin" refers to the thickness of the plate which is a relative relationship that is dependent upon the length and width of the plate, whereas for a cavity or hollow metal matrix composite or preform, "thin" refers to the thickness of  
25       the walls which define the cavity or hollow shell (i.e., the thickness of the walls are "thin" relative to the length, width or diameter of the metal matrix composite body containing the cavity or defined by the hollow shell). Further, "thin" refers to the relative thickness of the walls of the metal matrix composite which inversely replicate the configuration of the original  
30       matrix metal. However, in every embodiment, a "thin" dimensional characteristic must possess sufficient structural integrity to satisfy a particular end-use application.

#### Brief Description of the Drawings

30       The following Figures are provided to assist in understanding the invention, but are not intended to limit the scope of the invention. Similar reference numerals have been used wherever possible in each of the Figures to denote like components, wherein:

35       Figure 1 is a schematic cross-section of an assemblage of materials utilized to form two metal matrix composite bodies in accordance with Example 1;

Figure 2 is a photomicrograph at about 200X of the 500 grit 39 CRYSTOLON® green silicon carbide particulate used in Example 1;

Figure 3 is a photomicrograph at about 500X of the 500 grit 39 CRYSTOLON® green silicon carbide particulate used in Example 1;

5        Figure 4 is a photomicrograph at about 1000X of the 500 grit 39 CRYSTOLON® green silicon carbide particulate used in Example 1;

Figure 5 is a photomicrograph at about 200X of the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate used in Example 1;

10       Figure 6 is a photomicrograph at about 500X of the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate used in Example 1;

Figure 7 is a photomicrograph at about 1000X of the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate used in Example 1;

15       Figure 8 is a photomicrograph at about 3000X of the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate;

Figure 9 is a photograph of the two formed metal matrix composite bodies fabricated in Example 1;

20       Figure 10 is a photomicrograph at about 400X of the cross-section of the metal matrix composite body formed utilizing the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate in Example 1;

Figure 11 is a photomicrograph at about 400X of the cross-section of the metal matrix composite body formed utilizing the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate in Example 1;

25       Figure 12 is a graph depicting the average particle size distribution of the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate and the 500 grit 39 CRYSTOLON® green silicon carbide particulate used in Example 1;

30       Figure 13 is a cross-sectional schematic view of a lay-up employed in fabricating the highly loaded metal matrix composite ingot of Example 2, Sample A;

Figure 14A is a cross-sectional schematic view which shows the introduction of the highly loaded metal matrix composite material into the melt comprising the second matrix metal contained within a crucible and the

35



crushing of any loosely bound filler material from the highly loaded metal matrix composite;

Figure 14B is a cross-sectional schematic view which shows the introduction of a stirring means into the crucible containing molten first and second matrix metals in a crushed filler material of the highly loaded metal matrix composite material;

Figure 14C is a cross-sectional schematic view which shows a formed metal matrix composite suspension;

Figure 14D is a cross-sectional schematic view which shows the pouring of the metal matrix composite suspension from the crucible to form a cast metal matrix composite material;

Figure 15 is a cross-sectional schematic view of the stirrer/baffle assembly described in Example 2;

Figure 16 is a cross-sectional schematic view of the assembly used to cast the molten metal matrix composite suspension into the investment shell mold according to Example 2;

Figure 17 is a photograph of the cast metal matrix composite tensile bar and its attached gates and risers whose fabrication is described in Example 2;

Figure 18 is a graph showing melt fluidity as a function of melt temperature;

Figure 19 is a photomicrograph at about 1000X of a polished cross-section of Sample A material;

Figure 20 is a photomicrograph at about 1000X of a polished cross-section of Sample B material;

Figure 21 is a graph depicting the corrected flexural strength as a function of the test temperature of the metal matrix composite bodies, designated Samples C and D in Example 3 and the matrix AA 336.0 alloy, as a function of temperature. Additionally, Figure 21 also contains an estimate of the corrected flexural strength of a matrix metal corresponding substantially in composition to that of the matrix metal of Samples C and D of Example 3;

Figure 22 is a graph depicting the corrected flexural strength of metal matrix composite bodies, designated Samples E, F and G of Example 3, as well as matrix AA 336.0 alloy of Example 3, as a function of temperature;

Figure 23 is a photomicrograph at about 400X corresponding to Sample C of Example 3;

Figure 24 is a photomicrograph at about 400X corresponding to Sample D of Example 3;

Figure 25 is a photomicrograph at about 400X corresponding to Sample F of Example 3; and

5        Figure 26 is a photomicrograph at about 400X corresponding to Sample G in Example 3.

#### Detailed Description of the Preferred Embodiments

10        The filler materials of the present invention are intended to enhance the processing or formation of metal matrix composite bodies and/or improve resultant mechanical and/or physical properties of metal matrix composite bodies. These desirable aspects of the invention are achieved by utilizing filler materials having desirable morphologies (e.g., those filler materials which do not include any substantial number of high angle areas or sharp edges and are more rounded); and/or have an aspect ratio which is closer to "1" than  
15        other comparable filler materials; and/or contain a minimum number of surface flaws and critical flaws in the filler; and/or have a microroughness which increases the surface area of the filler relative to other comparable fillers; and/or have a desirable particle size distribution. Each of the above-  
20        discussed properties alone may enhance the production of metal matrix composite and/or improve resultant mechanical and/or physical properties of metal matrix composite bodies. However, when two or more of the above-discussed properties are combined in a single filler, the tendency to achieve enhanced production and/or enhanced properties in formed composite bodies  
25        increases. Thus, it is possible to utilize filler materials containing each of the above-discussed features so that the features synergistically interact to result in an extremely desirable filler and an extremely desirable resultant composite body.

30        While a substantial focus is made in this disclosure upon a particular metal matrix composite formation process known as "spontaneous infiltration," it should be understood that the filler material of the present invention should enhance virtually any metal matrix composite formation process. Such standard metal matrix composite formation processes include pressure casting, mixing of a filler material into a matrix metal, squeeze casting, etc. For  
35        example, by utilizing the filler material of the present invention, it may be possible to reduce the amount of time required to form a metal matrix

composite body; the processing temperature utilized to form a metal matrix composite body may be reduced; the ability to eliminate the need (or at least reduce the need) of wetting agents to assist the infiltration of matrix metal into a filler may be achieved; the need for complex and/or expensive apparatuses for formation of metal matrix composites may be eliminated; etc.

Still further, another important aspect of the filler material of the present invention is the ability of the filler material to flow in a dry state. For example, in many metal matrix composite formation processes it is first necessary to shape a filler material into a desirable shape. Such shaping may be effected by, for example, pouring a loose filler material mixture into a shaped mold and thereafter infiltrating, by any appropriate technique, the filler material with matrix metal. Thus, if a filler material is capable of being formed into any desirable shape without any substantial difficulties, the production of metal matrix composite bodies can be enhanced by shorter production times and/or lower production costs.

A particularly desirable filler material exhibiting many of the characteristics discussed above herein is shown in Figures 6-8. Particularly, Figures 6-8 are photomicrographs taken at various magnifications of a filler material known as 39 CRYSTOLON® Strong (Rounded) green silicon carbide manufactured by the Norton Company. This particular filler material has shown the ability to enhance the processing of metal matrix composite bodies made by a spontaneous infiltration technique. For example, the processing time required to infiltrate the filler material depicted in Figures 6-8 has been reduced relative to a similar filler material, as shown, for example, in Figure 4. Particularly, the grit size of the fillers in Figures 6-8 is substantially the same as the grit size in Figure 4; and the chemical compositions are substantially the same. Moreover, as discussed later herein, the properties of the formed metal matrix composite body are enhanced by utilization of the filler material of Figures 6-8. While significant emphasis is placed upon this particular filler material, it should be understood by those of ordinary skill in the art that filler materials having similar characteristics to those characteristics contained in the specific filler material discussed herein, whether or not having a substantially similar or substantially different chemical composition, should also exhibit desirable production characteristics and/or desirable properties in formed composite bodies.

Without wishing to be bound by any particular theory or explanation, it is possible that the filler material of the present invention enhances both production of metal matrix composite bodies and resultant properties in metal matrix composite bodies due to a number of effects including, for example, superior packing efficiency, more uniformly sized and shaped channels for matrix metal to infiltrate the filler, less stress concentration points in the formed composite body, etc.

In a preferred embodiment of the invention, the filler material is infiltrated by spontaneous infiltration. In order to effect spontaneous infiltration of the matrix metal into the filler material or preform, an infiltration enhancer should be provided to the spontaneous system. An infiltration enhancer could be formed from an infiltration enhancer precursor which could be provided (1) in the matrix metal; and/or (2) in the filler material or preform; and/or (3) from the infiltrating atmosphere; and/or (4) from an external source into the spontaneous system. Moreover, rather than supplying an infiltration enhancer precursor, an infiltration enhancer may be supplied directly to at least one of the filler material or preform, and/or matrix metal, and/or infiltrating atmosphere. Ultimately, at least during the spontaneous infiltration, the infiltration enhancer should be located in at least a portion of the filler material or preform.

In a preferred embodiment of the invention, it is possible that the infiltration enhancer precursor can be at least partially reacted with the infiltrating atmosphere such that the infiltration enhancer can be formed in at least a portion of the filler material or preform prior to or substantially contiguous with contacting the filler material or preform with the matrix metal (e.g., if magnesium was the infiltration enhancer precursor and nitrogen was the infiltrating atmosphere, the infiltration enhancer could be magnesium nitride which would be located in at least a portion of the preform or filler material).

An example of a matrix metal/infiltration enhancer precursor/infiltrating atmosphere system is the aluminum/magnesium/nitrogen system. Specifically, an aluminum matrix metal can be contained within a suitable refractory vessel which, under the process conditions, does not adversely react with the aluminum matrix metal and/or the filler material when the aluminum is made molten. A filler material or preform can thereafter be contacted with molten aluminum matrix metal and spontaneously infiltrated.

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Moreover, rather than supplying an infiltration enhancer precursor, an infiltration enhancer may be supplied directly to at least one of the preform or filler material, and/or matrix metal, and/or infiltrating atmosphere. Ultimately, at least during the spontaneous infiltration, the infiltration enhancer should be located in at least a portion of the filler material or preform.

Under the conditions employed in the method of the present invention, in the case of an aluminum/magnesium/nitrogen spontaneous infiltration system, the preform or filler material should be sufficiently permeable to permit the nitrogen-containing gas to penetrate or permeate the filler material or preform at some point during the process and/or contact the molten matrix metal. Moreover, the permeable filler material or preform can accommodate infiltration of the molten matrix metal, thereby causing the nitrogen-permeated preform to be infiltrated spontaneously with molten matrix metal to form a metal matrix composite body and/or cause the nitrogen to react with an infiltration enhancer precursor to form infiltration enhancer in the filler material or preform and thereby result in spontaneous infiltration. The extent of spontaneous infiltration and formation of the metal matrix composite will vary with a given set of process conditions, including magnesium content of the aluminum alloy, magnesium content of the preform or filler material, amount of magnesium nitride in the preform or filler material, the presence of additional alloying elements (e.g., silicon, iron, copper, manganese, chromium, nickel, titanium, zinc, and the like), average size of the filler material (e.g., particle diameter) comprising the preform or the filler material, surface condition and type of filler material or preform, nitrogen concentration of the infiltrating atmosphere, time permitted for infiltration and temperature at which infiltration occurs. For example, for infiltration of the molten aluminum matrix metal to occur spontaneously, the aluminum can be alloyed with at least about 0.1 percent by weight, and preferably at least about 1-3 percent by weight, magnesium (which functions as the infiltration enhancer precursor), based on alloy weight. Auxiliary alloying elements, as discussed above, may also be included in the matrix metal to tailor specific properties thereof. Additionally, the auxiliary alloying elements may affect the minimum amount of magnesium required in the matrix aluminum metal to result in spontaneous infiltration of the filler material or preform. Loss of magnesium from the spontaneous system due to, for example, volatilization

should not occur to such an extent that no magnesium was present to form infiltration enhancer. Thus, it is desirable to utilize a sufficient amount of initial alloying elements to assure that spontaneous infiltration will not be adversely affected by volatilization. Still further, the presence of  
5 magnesium in both of the preform (or filler material) and matrix metal or the preform (or filler material) alone may result in a reduction in the required amount of magnesium to achieve spontaneous infiltration (discussed in greater detail later herein).

The volume percent of nitrogen in the infiltrating atmosphere also  
10 affects formation rates of the metal matrix composite body. Specifically, if less than about 10 volume percent of nitrogen is present in the atmosphere, very slow or little spontaneous infiltration will occur. It has been discovered that it is preferable for at least about 50 volume percent of  
15 nitrogen to be present in the atmosphere, thereby resulting in, for example, shorter infiltration times due to a much more rapid rate of infiltration. The infiltrating atmosphere (e.g., a nitrogen-containing gas) can be supplied directly to the filler material or preform and/or matrix metal, or it may be produced or result from a decomposition of a material.

The minimum magnesium content required for the molten matrix metal to  
20 infiltrate a filler material or preform depends on one or more variables such as the processing temperature, time, the presence of auxiliary alloying elements such as silicon or zinc, the nature of the filler material, the location of the magnesium in one or more components of the spontaneous system, the nitrogen content of the atmosphere, and the rate at which the nitrogen  
25 atmosphere flows. Lower temperatures or shorter heating times can be used to obtain complete infiltration as the magnesium content of the alloy and/or preform is increased. Also, for a given magnesium content, the addition of certain auxiliary alloying elements such as zinc permits the use of lower temperatures. For example, a magnesium content of the matrix metal at the  
30 lower preferred end of the operable range, e.g., from about 1 to 3 weight percent, may be used in conjunction with at least one of the following: an above-minimum processing temperature, a high nitrogen concentration, or one or more auxiliary alloying elements. When no magnesium is added to the preform, alloys containing from about 3 to 5 weight percent magnesium are preferred on  
35 the basis of their general utility over a wide variety of process conditions, with at least about 5 percent being preferred when lower temperatures and

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shorter times are employed. Magnesium contents in excess of about 10 percent by weight of the aluminum alloy may be employed to moderate the temperature conditions required for infiltration. The magnesium content may be reduced when used in conjunction with an auxiliary alloying element, but these elements serve an auxiliary function only and are used together with at least the above-specified minimum amount of magnesium.

As a further example, the amount of magnesium varies if it is supplied exclusively to the preform or filler material. It has been discovered that spontaneous infiltration will occur with a lesser weight percent of magnesium supplied to the spontaneous system when at least some of the total amount of magnesium supplied is placed in the preform or filler material. It may be desirable for a lesser amount of magnesium to be provided in order to prevent the formation of undesirable intermetallics in the metal matrix composite body. In the case of a silicon carbide preform, it has been discovered that when the preform is contacted with an aluminum matrix metal, the preform containing at least about 1% by weight magnesium and being in the presence of a substantially pure nitrogen atmosphere, the matrix metal spontaneously infiltrates the preform. In the case of an alumina preform, the amount of magnesium required to achieve acceptable spontaneous infiltration is slightly higher. Specifically, it has been found that when an alumina preform is contacted with a similar aluminum matrix metal, at about the same temperature as the aluminum that infiltrated into the silicon carbide preform, and in the presence of the same nitrogen atmosphere, at least about 3% by weight magnesium may be required to achieve similar spontaneous infiltration to that achieved in the silicon carbide preform discussed immediately above.

It is also noted that it is possible to supply to the spontaneous system infiltration enhancer precursor and/or infiltration enhancer on a surface of the alloy and/or on a surface of the preform or filler material and/or within the preform or filler material prior to infiltrating the matrix metal into the filler material or preform (i.e., it may not be necessary for the supplied infiltration enhancer or infiltration enhancer precursor to be alloyed with the matrix metal, but rather, simply supplied to the spontaneous system). For example, in the aluminum/magnesium/nitrogen system, if the magnesium was applied to a surface of the matrix metal it may be preferred that the surface should be the surface which is closest to, or preferably in contact with, the permeable mass of filler material or vice versa; or such magnesium could be

mixed into at least a portion of the preform or filler material. Still further, it is possible that some combination of surface application, alloying and placement of magnesium into at least a portion of the preform could be used. Such combination of applying infiltration enhancer(s) and/or  
5 infiltration enhancer precursor(s) could result in a decrease in the total weight percent of magnesium needed to promote infiltration of the matrix aluminum metal into the preform, as well as achieving lower temperatures at which infiltration can occur. Moreover, the amount of undesirable intermetallics formed due to the presence of magnesium could also be  
10 minimized.

The use of one or more auxiliary alloying elements and the concentration of nitrogen in the surrounding gas also affects the extent of nitriding of the matrix metal at a given temperature. For example, auxiliary alloying elements such as zinc or iron included in the alloy, or placed on a surface of the  
15 alloy, may be used to reduce the infiltration temperature and thereby decrease the amount of nitride formation, whereas increasing the concentration of nitrogen in the gas may be used to promote nitride formation.

The concentration of magnesium in the alloy, and/or placed onto a surface of the alloy, and/or combined in the filler or preform material, also  
20 tends to affect the extent of infiltration at a given temperature. Consequently, in some cases where little or no magnesium is contacted directly with the preform or filler material, it may be preferred that at least about three weight percent magnesium be included in the alloy. Alloy contents of less than this amount, such as one weight percent magnesium, may require  
25 higher process temperatures or an auxiliary alloying element for infiltration. The temperature required to effect the spontaneous infiltration process of this invention may be lower: (1) when the magnesium content of the alloy alone is increased, e.g., to at least about 5 weight percent; and/or (2) when alloying constituents are mixed with the permeable mass of filler material or  
30 preform; and/or (3) when another element such as zinc or iron is present in the aluminum alloy. The temperature also may vary with different filler materials. In general, in the aluminum/magnesium/nitrogen system spontaneous and progressive infiltration will occur at a process temperature of at least about 650°C, and preferably a process temperature of at least about 750°C-  
35 850°C. Temperatures generally in excess of 1200°C do not appear to benefit the process, and a particularly useful temperature range has been found to be



from about 675°C to about 1050°C. However, as a general rule, the spontaneous infiltration temperature is a temperature which is above the melting point of the matrix metal but below the volatilization temperature of the matrix metal. Moreover, the spontaneous infiltration temperature should be below the melting point of the filler material. Still further, as temperature is increased, the tendency to form a reaction product between the matrix metal and infiltrating atmosphere increases (e.g., in the case of aluminum matrix metal and a nitrogen infiltrating atmosphere, aluminum nitride may be formed). Such reaction product may be desirable or undesirable based upon the intended application of the metal matrix composite body. Additionally, electric resistance heating is typically used to achieve the infiltrating temperatures. However, any heating means which can cause the matrix metal to become molten and does not adversely affect spontaneous infiltration, is acceptable for use with the invention.

In the present method, for example, a permeable filler material or preform comes into contact with molten aluminum in the presence of, at least sometime during the process, a nitrogen-containing gas. The nitrogen-containing gas may be supplied by maintaining a continuous flow of gas into contact with at least one of the filler material or preform and/or molten aluminum matrix metal or by containing the filler material or preform in a closed or static atmospheric system. Although the flow rate of the nitrogen-containing gas is not critical (e.g., flowing nitrogen may not even be essential), it is preferred that a flow rate be established such that, for example, the flow rate is sufficient to compensate for any nitrogen lost from the atmosphere due to any nitride formation, and also to prevent or inhibit the incursion of air which can have an oxidizing effect on the molten metal.

Many different combinations of matrix metals (e.g., aluminum, magnesium, silicon, titanium, copper, bronze, cast iron, hafnium, etc.) can be combined with many different filler materials (e.g., oxides, carbides, borides, nitrides, etc.) of the present invention to form numerous metal matrix composite bodies. For example, when aluminum is the matrix metal, suitable filler materials include (a) oxides, e.g. alumina, magnesia, zirconia etc.; (b) carbides, e.g. silicon carbide; (c) borides, e.g. aluminum dodecaboride, titanium diboride; and (d) nitrides, e.g. aluminum nitride, silicon nitride; and (e) mixtures thereof. If there is a tendency for the filler material to react with the molten aluminum matrix metal, this might be accommodated by

minimizing the infiltration time and temperature or by providing a non-reactive coating on the filler. The filler material may comprise a substrate, such as carbon or other non-ceramic material, bearing a ceramic coating to protect the substrate from attack or degradation. Suitable ceramic coatings include oxides, carbides, borides and nitrides. Ceramics which are preferred for use in the present method include alumina and silicon carbide.

The method of forming a metal matrix composite is applicable to a wide variety of filler materials, and the choice of filler materials will depend on such factors as the matrix alloy, the process conditions, the reactivity of the molten matrix alloy with the filler material, and the properties sought for the final composite product.

A barrier means may also be utilized in combination with the present invention. Specifically, the barrier means for use with this invention may be any suitable means which interferes, inhibits, prevents or terminates the migration, movement, or the like, of molten matrix alloy (e.g., an aluminum alloy) beyond the defined surface boundary of the filler material. Suitable barrier means may be any material, compound, element, composition, or the like, which, under the process conditions of this invention, maintains some integrity, is not volatile and preferably is permeable to the gas used with the process, as well as being capable of locally inhibiting, stopping, interfering with, preventing, or the like, continued infiltration or any other kind of movement beyond the defined surface boundary of the ceramic filler. Barrier means may be used during spontaneous infiltration or in any molds or other fixtures utilized in connection with thermo-forming of the spontaneously infiltrated metal matrix composite, as discussed in greater detail below.

Suitable barrier means includes materials which are substantially non-wettable by the migrating molten matrix alloy under the process conditions employed. A barrier of this type appears to exhibit little or no affinity for the molten matrix alloy, and movement beyond the defined surface boundary of the filler material or preform is prevented or inhibited by the barrier means. The barrier reduces any final machining or grinding that may be required of the metal matrix composite product. As stated above, the barrier preferably should be permeable or porous, or rendered permeable by puncturing, to permit the gas (e.g., infiltrating atmosphere) to contact the molten matrix alloy.

Suitable barriers particularly useful for aluminum matrix alloys are those containing carbon, especially the crystalline allotropic form of carbon

known as graphite. Graphite is essentially non-wettable by the molten aluminum alloy under the described process conditions. Particular preferred graphites are graphite foil products that are sold under the trademark GRAFOIL®, registered to Union Carbide and PERMA-FOIL™, distributed by  
5 TTAmerica. These graphite foils exhibit sealing characteristics that prevent the migration of molten aluminum alloy beyond the defined surface boundary of the filler material. These graphite foils are also resistant to heat and are chemically inert. GRAFOIL® graphite foil and PERMA-FOIL™ graphite foil are flexible, compatible, conformable and resilient. They can be made into a  
10 variety of shapes to fit any barrier application. GRAFOIL® graphite foil and PERMA-FOIL™ graphite foil are particularly preferred because they are in the form of a flexible graphite sheet. In use, these paper-like graphites are simply formed around the filler material or preform. Moreover, in addition to or in combination with graphite foils, other graphite barrier means may be  
15 employed as a colloidal graphite suspension, a slurry or paste or even as a paint film around and on the boundary of the filler material or preform.

Other preferred barrier(s) for aluminum metal matrix alloys in nitrogen are the transition metal borides (e.g., titanium diboride ( $TiB_2$ )) which are generally non-wettable by the molten aluminum metal alloy under certain of the  
20 process conditions employed when using this material. With a barrier of this type, the process temperature should not exceed about 875°C, for otherwise the barrier material becomes less efficacious and, in fact, with increased temperature infiltration into the barrier will occur. Moreover, the particle size of the barrier material may affect the ability of the material to inhibit  
25 spontaneous infiltration. The transition metal borides are typically in a particulate form (1-30 microns). The barrier materials may be applied as a slurry or paste to the boundaries of the permeable mass of ceramic filler material which preferably is preshaped as a preform.

Other useful barriers for aluminum metal matrix alloys in nitrogen  
30 include low-volatile organic compounds applied as a film or layer onto the external surface of the filler material or preform. Upon firing in nitrogen, especially at the process conditions of this invention, the organic compound decomposes leaving a carbon soot film. The organic compound may be applied by conventional means such as painting, spraying, dipping, etc.

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Moreover, finely ground particulate materials can function as a barrier so long as infiltration of the particulate material would occur at a rate which is slower than the rate of infiltration of the filler material.

Thus, the barrier means may be applied by any suitable means, such as by covering the defined surface boundary with a layer of the barrier means. Such a layer of barrier means may be applied by painting, dipping, silk screening, evaporating, or otherwise applying the barrier means in liquid (e.g., colloidal graphite suspension), slurry, or paste form, or by sputtering a vaporizable barrier means, or by simply depositing a layer of a solid particulate barrier means, or by applying a solid thin sheet or film of barrier means onto the defined surface boundary. With the barrier means in place, spontaneous infiltration substantially terminates when the infiltrating matrix metal reaches the defined surface boundary and contacts the barrier means.

Various demonstrations of the present invention are included in the Examples immediately following. However, these Examples should be considered as being illustrative and should not be construed as limiting the scope of the invention as defined in the appended claims.

#### 20 Example 1

This Example demonstrates that by utilizing 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate (Norton Company, Worcester, MA) as a filler material, the surface finish of an as-fabricated metal matrix composite body can be demonstrably improved relative to a metal matrix composite body which contains a "standard" 39 CRYSTOLON® green silicon carbide particulate. Moreover, porosity throughout the metal matrix composite body may be decreased relative to a metal matrix composite body which contains a "standard" 39 CRYSTOLON® green silicon carbide particulate. Specifically, two metal matrix composite bodies were fabricated under substantially identical processing conditions. However, one body was fabricated utilizing the 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate as a filler, and the other metal matrix composite body was fabricated utilizing "standard" 39 CRYSTOLON® green silicon carbide particulate as a filler.

About 2000 grams of 500 grit 39 CRYSTOLON® green silicon carbide particulate (Norton Company, Worcester, MA), about 4000 grams of 1/2 inch (13 mm) by 1/2 inch (13 mm) cylindrical alumina grinding media and about 60 grams of -325 mesh magnesium powder (Hart Corporation, Tamaqua, PA) were added to a

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5 liter NALGENE® plastic jar (Nalge Company, Rochester, NY). The jar was sealed and the contents were mixed by vigorously shaking the jar by hand for about 30 seconds. The contents of the NALGENE® plastic jar were then transferred to a porcelain jar. The porcelain jar and its contents were placed on a jar mill and mixed for about 2 hours. The porcelain jar was removed from the jar mill and the contents of the jar was poured through a coarse sieve such that the silicon carbide/magnesium mixture passed through the sieve and into a stainless steel container and the alumina grinding media was retained by the sieve.

A temperature of about 150°C was established within a drying oven. The stainless steel container and its contents were placed within the drying oven, the drying oven was sealed and a vacuum level of about 29 inches (737 mm) of mercury was established within the oven. After heating the stainless steel container and its contents for about 12 hours at a temperature of about 150°C and a vacuum of about 29 inches (737 mm) of mercury, atmospheric pressure was reestablished in the drying oven, and the stainless steel container and its contents were removed from the oven. The silicon carbide/magnesium mixture was placed into a NALGENE® plastic jar and remixed by physically shaking the jar by hand.

A second silicon carbide/magnesium mixture was prepared in essentially the same manner as described above except that 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate (Norton Company, Worcester, MA) was used instead of 500 grit 39 CRYSTOLON® green silicon carbide. Table I, described in greater detail below, characterizes certain properties of the 500 grit 39 CRYSTOLON® green silicon carbide particulate and the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate.

As shown in Figure 1, two graphite foil boxes 2 measuring about 3 inches (76 mm) square and about 3 inches (76 mm) high were fabricated from a single sheet of GRAFOIL® graphite foil (Union Carbide Company, Danbury, CT) measuring about 0.015 inch (0.38 mm) thick by making strategically located cuts and folds in the sheet. Strategically placed staples helped to reinforce the folds in the GRAFOIL® sheet. Each GRAFOIL® graphite foil box 2 was then placed within a graphite boat 1 having substantially the same dimensions as the GRAFOIL® graphite foil box 2.

About 225 grams of the 39 CRYSTOLON® Strong (Rounded) green silicon carbide/magnesium mixture 3r was poured into one GRAFOIL® box 2. About 225

grams of the "standard" 39 CRYSTOLON® green silicon carbide/magnesium mixture 3s was poured into the second GRAFOIL® box 2. To assist in the settling of the mixtures, each graphite boat 1 was moved in a side to side manner several times and then light hammer taps were applied to the sides of each graphite boat 1. A foam brush was used to establish a level surface of silicon carbide/magnesium mixture within each GRAFOIL® box 2. About 1.12 grams of -24 mesh (particle diameter less than about 701 microns) Mg powder 4 (Hart Corporation, Tamaqua, PA) was sprinkled onto the top surface of the 39 CRYSTOLON® Strong (Rounded) green silicon carbide/magnesium mixture 3r within the first GRAFOIL® box 2. About 1.15 grams of -24 mesh (particle diameter less than about 701 microns) Mg powder 4 was sprinkled onto the top portion of the "standard" 39 CRYSTOLON® green silicon carbide/magnesium mixture 3s within the second GRAFOIL® box 2. Two ingots of matrix metal 5; each measuring about 3 inches (76 mm) square by about 1 inch (25 mm) thick, having a combined weight of about 415.65 grams and comprising by weight about 12 percent Si and the balance Al, were placed into the first GRAFOIL® box 2 and onto the top surface of the 39 CRYSTOLON® Strong (Rounded) green silicon carbide/magnesium mixture 35 and in contact with the -24 mesh Mg powder 4. This procedure was repeated for the second GRAFOIL® box 2 except that the ingots of matrix metal 5 had a combined weight of about 414.68 grams.

Both graphite boats 1 and their contents were placed onto a larger graphite catcher plate 6. The graphite catcher plate 6, the graphite boats 1 and their contents were then placed within a resistance heated controlled atmosphere furnace. The furnace was sealed and evacuated to about 30 inches (762 mm) of mercury vacuum. The furnace was backfilled with nitrogen gas to a pressure of about 1 pound per square inch (0.0703 Kg/cm<sup>3</sup>). The nitrogen gas flow was interrupted and the furnace was evacuated to about 30 inches (762 mm) of mercury vacuum. The furnace was backfilled with nitrogen gas to about atmospheric pressure and a nitrogen gas flow rate of about 4 liters per minute was established within the furnace. The temperature within the furnace was increased from about room temperature to about 780°C in about 4 hours. After maintaining a temperature of about 780°C for about 4 hours, the graphite boats 1 and their contents were removed from the furnace and placed onto a water-cooled copper chill plate.

When the graphite boats 1 and their contents reached about room temperature, the formed metal matrix composite bodies were removed from the

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graphite boats 1 and the GRAFOIL® boxes 2. Figure 9 is a photograph of the two formed metal matrix composite bodies with the surface of the bodies that had been in contact with the bottom of the GRAFOIL® boxes 2 facing up. The metal matrix composite body marked with the number 1 was fabricated with the 500 grit (average particle diameter of about 15.6 microns) 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate, and the metal matrix composite body marked with the number 2 was fabricated utilizing the 500 grit (average particle diameter of about 17 microns) 39 CRYSTOLON® green silicon carbide particulate. As can be seen from Figure 9, composite body number 1 has a smoother surface with less porosity than composite body number 2. Thus, this Example demonstrates that an improved surface finish of a metal matrix composite body may be obtained by utilizing 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate as a filler material, as compared to a "standard" 500 grit 39 CRYSTOLON® green silicon carbide particulate.

The formed metal matrix composite bodies were subsequently cross sectioned, mounted, polished and subjected to quantitative image analysis utilizing the QUANTIMET 520 Image Analysis System (Cambridge Instruments, Ltd., Cambridge, CB1 3QH, England). The system consists of: a microscope fitted with a motorized stage, motorized focus, and TV camera; a TV monitor; a Compaq 386/20e computer with image analysis software; and a Cambridge computer fitted with special function boards that handle the various automation and image processing tasks.

The QUANTIMET 520 is operated in the following manner:

First, the analyst obtains a well-polished sample and places it on the center of the motorized stage, then focuses using the TV monitor. By moving the sample on the motorized stage using a control lever, the analyst then defines the upper left and lower right corners of the rectangular area to be analyzed. The stage then automatically moves to the center of the sample where range of focus is initialized.

Second, the stage moves to the right side of the sample, the microscope focuses on the sample, and the computer prompts for the number of phases, their names and the percentage of the total area to analyze. Three phases (metal, filler, pores) are analyzed and a percentage is chosen that provides at least 200 images, depending on magnification. The phases are then defined by gray levels (each black and white image is segmented into 256 gray levels, therefore, each phase is some portion of that scale (0-255)). Once each phase

is defined, the stage moves to the left side of the sample and the phases' gray levels are determined again. The second step is added to account for any variation across the sample.

Finally, the sample is ready to be analyzed. The stage moves back to the upper left corner. The computer automatically calculates the distance to move the stage to provide the specified percentage of the area defined by the two corners. At each image, focus on the sample occurs automatically, as does the measurement of the area of each phase. After all images are analyzed, a printout of area percents and standard deviation of each phase is generated.

Table I lists the results of the image analysis performed on the two (2) cross-sectioned metal matrix composite bodies of this Example. Sample 1 indicates the results obtained from the metal matrix composite body fabricated utilizing the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate and Sample 2 indicates the results obtained from the metal matrix composite body fabricated utilizing the 500 grit 39 CRYSTOLON® green silicon carbide particulate.

TABLE I  
Quantitative Image Analysis

20	SAMPLE 1:*	Phases:	Filler	Metal	Pores
		Area:	65.871	30.825	3.304
		+/-:	2.956	4.207	2.880
25	SAMPLE 2:**	Phases:	Filler	Metal	Pores
		Area:	43.316	26.298	30.385
		+/-:	17.508	12.096	28.539

\*(Total area analyzed = 3.27433 mm<sup>2</sup>; average phase % after 228 frames; magnification = 500X)

\*\* (Total area analyzed = 3.360496 mm<sup>2</sup>; average phase % after 234 frames; magnification = 500X)

Figure 10 is a photomicrograph at 400X of the cross-section of the metal matrix composite body formed utilizing the 500 grit 39 CRYSTOLON® Strong (Rounded) silicon carbide particulate. Figure 11 is a photomicrograph at 400X of the cross-section of the metal matrix composite body formed utilizing the



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500 grit 39 CRYSTOLON® green silicon carbide particulate. In each of Figures 10 and 11, the light areas are matrix metal, the gray areas are silicon carbide, and the dark areas are porosity.

5 This Example demonstrates that by utilizing 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide as a filler material, a metal matrix composite body with improved surface finish and reduced porosity may be fabricated.

10 The parameters chosen for this Example clearly demonstrate the advantages of the present invention. Moreover, it should be noted that by changing any single parameter or any number of parameters (i.e., increase or decrease Mg addition, increase or decrease infiltration temperature, etc.), the properties (e.g., surface finish, porosity, etc.) of the metal matrix composite body may be altered (e.g., improved). However, under these processing conditions it is clear that a metal matrix composite body formed  
15 utilizing the 39 CRYSTOLON® Strong (Rounded) silicon carbide particulate will have improved surface finish and reduced porosity when compared to a metal matrix composite body formed in the same manner utilizing "standard" 39 CRYSTOLON® green silicon carbide particulate.

20 Table II shows a comparison of certain properties of 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particles and 500 grit "standard" 39 CRYSTOLON® green silicon carbide, as well as 400 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate and 800 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate. Moreover,  
25 Figures 2, 3 and 4 are photomicrographs at 200X, 500X and 1000X, respectively, of the 500 grit 39 CRYSTOLON® green silicon carbide particulate. Figures 5, 6, 7 and 8 are photomicrographs at 200X, 500X and 1000X and 3000X, respectively, of the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate.

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TABLE II

	500 Grit 39 CRYSTOLON® Green Silicon Carbide	500 Grit 39 CRYSTOLON® Strong (Rounded) Green Silicon Carbide	400 Grit 39 CRYSTOLON® Strong (Rounded) Green Silicon Carbide	800 Grit 39 CRYSTOLON® Strong (Rounded) Green Silicon Carbide
Tap density (g/cm <sup>3</sup> )	1.70	1.92	2.00	1.67
Mean particle diameter (μm)	17.4	15.6	19.7	8.3
Surface area (m <sup>2</sup> /g)	0.42	0.76	0.34	0.96

The tap density of each of the silicon carbide particulate materials was measured by placing about 50 grams of the silicon carbide particulate into a graduated cylinder. The graduated cylinder was placed onto a Tap-Pak volumeter (marketed by Shandon Southern Instruments Inc., Sewickley, PA) and subjected to 3000 taps. The volume of the tapped particulate was measured, and the weight of the particulate was divided by the volume to determine the tap density of the silicon carbide particulate. As can be seen from Table II, the tap density of the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate is greater than the tap density of the 500 grit 39 CRYSTOLON® green silicon carbide particulate.

The mean particle diameter of the silicon carbide particulate was measured utilizing a MICROTRAC® Model 7995-10 Particle Size Analyzer (Leeds & Northrop, North Wales, PA). Specifically, the SRA/SBA button was set to SRA. The number of runs was set at 3 and the run time was set at 50 seconds. The dV check button was pushed, and a reading of about 0.0000 was recorded. With the dV check on, the sample of silicon carbide particulate was added gradually until the dV value reached its peak and began to rapidly decrease. The peak dV value was noted and a small quantity of silicon carbide particulate was removed. Water was added to dilute the sample so that the dV value dropped to about 20% below the peak dV value. The "cancel" button was depressed. At this point, the run button was depressed and the analysis was performed. A total of 3 analyses were performed and an average value was obtained. The mean particle diameter of the 500 grit 39 CRYSTOLON® green silicon carbide particulate, and the 500 grit, 400 grit and 800 grit 39 CRYSTOLON® green silicon carbide are shown in Table II.

Figure 12 shows, in graph format, the average particle size distribution of the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate (indicated by the cross-hatched bars) compared to the average particle size distribution of the 500 grit 39 CRYSTOLON® green silicon carbide particulate (indicated by the solid bars).

The surface area of the silicon carbide particulate was measured utilizing a Model 4200 Automatic Surface Area Analyzer (Leeds & Northrop, North Wales, PA). Specifically, the silicon carbide particulate was prepared by filling the cell on the analyzer with silicon carbide particulate to a level of approximately 1/3 the height of the cell. The cell was installed in

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the prep station and the heat was adjusted to about 200°C. The cell containing the silicon carbide particulate was placed in the test station and liquid nitrogen was added to a level of about 1/2 inch (13 mm) from the top of the cell. The motor was turned on, the mode of the analyzer was set to automatic and the adsorb switch was turned on. After approximately 70 seconds, the contents of the cell were weighed and the weight was recorded. As shown in Table II, the 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate had a surface area of almost twice that of the 500 grit 39 CRYSTOLON® green silicon carbide particulate.

#### Example 2

This Example compares and contrasts certain characteristics of two castable metal matrix composite materials. The first, Sample A, is prepared from a precursor highly loaded metal matrix composite melt comprising a strong (e.g., rounded) silicon carbide particulate filler material. The highly loaded metal matrix composite material is prepared by a spontaneous infiltration process and subsequently diluted with additional matrix metal such that the diluted, castable metal matrix composite melt comprises by weight about 20 percent silicon carbide filler material. The castable metal matrix composite material to which the Sample A material is to be compared consists of a DURALCAN™ castable metal matrix composite material, denoted as Sample B, which also comprises by weight about 20 percent silicon carbide particulate filler material. The silicon carbide filler material of Sample B, however, was of the blocky, angular morphology which is usually typical of alpha silicon carbide.

#### Sample A Material

A highly loaded metal matrix composite was fabricated as follows and as shown in Figure 13.

A filler material mixture 25 comprising about 1500 grams of 500 grit 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate (Norton Co., Worcester, MA), having an average particle size of about 15.6 microns, and about 45 grams of -325 mesh (particle diameter less than about 45 microns) magnesium powder (Hart Corporation, Tamaqua, PA) was ball milled for about an hour in an approximately 8 liter porcelain ball mill containing about 3100 grams of about 1 inch (25 mm) diameter alumina stones.

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The ball milled mixture 25 was then vacuum dried for about 24 hours at a temperature of about 225°C. A number of batches of this processed filler material mixture were made according to the above procedure to provide a sufficient quantity of filler material mixture for the quantity of castable metal matrix composite material desired.

The vessel 80 used for housing the filler material mixture 25 and matrix metal during fabrication of the highly loaded metal matrix composite comprised a steel tube measuring about 5 1/2 inches (140 mm) in diameter by about 3 feet (0.9 meters) long. The steel tube 80 was closed on one end and was lined on its interior surface with about 3 layers of GRAFOIL® graphite foil 82 (Union Carbide Company, Carbon Products Division, Cleveland, OH). About 25 lbs (11.35 kilograms) of the filler material mixture 25 was poured into the lined steel vessel 80, levelled and settled. Magnesium particulate 34 (-325 mesh, Hart Corporation) was then sprinkled evenly over the top surface of the filler material 25 until a concentration of about 16 milligrams per square centimeter of magnesium particulate was achieved.

The steel vessel 80 and its contents were then placed into a resistance heated air atmosphere furnace at about room temperature. A nitrogen gas purge tube 44 was supplied to the interior of the steel vessel 80 terminating near the opening at the top of the vessel 80. Copper sheet 42 was then placed around the purge tube 44 and the opening of the steel vessel 80 to effect a loose seal around the purge tube 44 and the upper portion of the steel vessel 80, but sufficient to maintain a substantially nitrogenous atmosphere in the steel vessel 80 during subsequent heating. Commercially pure nitrogen was provided to the system and a nitrogen gas flow rate of about 30 liters per minute into the stainless steel vessel 80 was established. The nitrogen gas exited at the loose fitting junctions where the copper sheet 42 met the purge tube 44 and the lip of the stainless steel vessel 80.

The top cover of the furnace was placed onto the furnace, and the furnace was heated to a temperature of about 225°C at a rate of about 400°C per hour. After maintaining a temperature of about 225°C for about 12 hours, the temperature was then increased to about 750°C at a rate of about 400°C per hour. After maintaining a temperature of about 750°C for about 1 1/2 hours, the top cover of the furnace was removed, the copper sheet was removed and about 22.7 kilograms of a molten matrix metal (not shown in the Figures) comprising about 12 weight percent silicon and the balance aluminum was poured

into the lined stainless steel vessel 80 on top of the filler material admixture 25. The molten matrix metal began to spontaneously infiltrate the filler material admixture 25 almost immediately. The matrix metal was added in increments so as to be able to gauge more easily the progress of spontaneous infiltration. After the last increment of metal had been added, the stainless steel vessel 80 and its contents were held in the furnace at a temperature of about 750°C for an additional approximately five minutes. Power to the furnace was then interrupted and the furnace and its contents were allowed to cool back to room temperature.

The stainless steel vessel 80 was cut open and the layers of GRAFOIL® graphite foil 82 were removed to reveal that the matrix metal had infiltrated the filler material admixture 25 to form a highly loaded metal matrix composite ingot. The excess uninfiltrated matrix metal at the top of the ingot was removed with a diamond saw, and the exterior surface of the highly loaded metal matrix composite ingot was cleaned by grit blasting.

A STARRBIDE® #70 bilge crucible (American Refractories and Crucible Corp., North Haven, CT) whose interior measured about 18 inches (457 mm) deep and about 12 inches (305 mm) in diameter was placed into a resistance heated air atmosphere furnace such that the lip of the crucible was substantially flush with the top surface of the furnace. The crucible was then heated to a temperature of about 540°C. About 36.0 lbs (16.3 kilograms) of a second matrix metal 202 (See Figure 14a) comprising by weight about 10 percent silicon and the balance aluminum was then placed into the bilge crucible. An argon cover gas was introduced into the opening of the crucible at a flow rate of about 10 liters per minute. The opening at the top of the crucible was covered with an approximately 2 inch (51 mm) thick layer of FIBERFRAX® ceramic fiber insulating material (Carborundum Co., Niagara Falls, NY) while the crucible contents were prepared for casting.

The crucible and its contents were then heated from a temperature of about 540°C to a temperature of about 720°C at a rate of about 45°C per hour under the flowing argon cover gas. During this heating period, an investment shell mold having a shape and composition typical for the industry was fabricated so as to cast a tensile bar shape therein. The mold was further prepared for the casting operation by placing the mold into an air atmosphere furnace at a temperature of about 750°C for about 20 minutes to burn out any residual wax remaining from the investment patterns. The mold was then

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transferred to an air atmosphere furnace at a temperature of about 875°C to rigidize the mold and to volatilize any residual impurities in the mold. After maintaining the investment shell mold at a temperature of about 875°C for about 1 hour, the mold was transferred to an air atmosphere furnace at a temperature of about 540°C, where it was held until the molten metal matrix composite material was ready to be cast.

When the crucible and its contents had reached a temperature of about 722°C, an approximately 14.15 lb. (6.43 kg) piece of the highly loaded metal matrix composite ingot described earlier in this Example was added to the molten second matrix metal. After about an hour, the temperature of the contents of the crucible had recovered to about 702°C. As shown in Figure 14a, a stainless steel rod 206 was inserted into the formed metal matrix composite suspension to break down any remaining clumps from the added highly loaded metal matrix composite ingot fragment 204. After about an additional 25 minutes, the temperature of the suspension had dropped to about 643°C. The added metal matrix composite material 204 had been fairly well broken up by crushing with the stainless steel rod 206, and thus an additional approximately 7.35 lb. (3.34 kg) quantity of the aforementioned highly loaded metal matrix composite ingot material 204 was added to the crucible. After about 35 additional minutes, the temperature of the suspension had recovered to about 668°C, and the stainless steel rod 206 was again inserted into the crucible 200 to break up residual undispersed parts of the second piece of the highly loaded metal matrix composite ingot material 204. After about 15 more minutes, the temperature of the suspension was about 640°C, and the second addition of highly loaded metal matrix composite ingot material appeared to be well dispersed. The stirrer/baffle assembly shown in Figure 15 was then lowered to just above the surface of the suspension to preheat the assembly to a temperature of about 300°C. The impeller 100 measured about 4 inches (102 mm) in diameter and comprised Grade AFX-5Q graphite (Poco Graphite Inc., Decatur, TX) which was coated with a thin layer comprising titanium carbide substantially in accordance with the method described in applicants' commonly owned and copending U.S. Patent Application Serial No. 07/543,316, filed June 25, 1990 (corresponding to International Application No. PCT/US91/04762, filed June 25, 1991, and published on January 9, 1992, as International Publication No. WO 92/00256). The coated impeller was connected to an approximately one half horsepower air-driven motor 102 (Eclipse Systems, Inc., Franklin, NJ) by

means of a graphite shaft 104 measuring about 1 1/2 inches (32 mm) in diameter by about 3 feet (0.9 meter) long. The preheated stirrer/baffle assembly 208 was then lowered into the suspension and stirring commenced, as illustrated in Figure 14b. After stirring the suspension 210 for about 10 minutes at an  
5 impeller speed of about 2500 rpm, stirring was ceased and the stirrer/baffle assembly 208 was removed from the suspension 210. A foam which had formed on the surface of the suspension 210 was removed along with the surface dross by means of a hand-held skimmer which had been coated with ZIRCWASH® mold wash (ZYP Coatings, Oak Ridge, TN) (not shown in Figure). The suspension 210 was  
10 then stirred by hand with the coated skimmer, which revealed the presence of several approximately 0.5 inch (13 mm) diameter pieces of undispersed highly loaded metal matrix composite ingot material 204. Accordingly, the stirrer/baffle assembly 208 was lowered back into the approximately 658°C suspension 210 and the suspension was stirred for about 10 minutes at an  
15 impeller speed of about 1500 rpm. The stirrer was again stopped and the assembly 208 was raised from the suspension 210. The temperature of the suspension 210 was now about 630°C. At this temperature, two fluidity samples were taken, the procedural description of which is described in a subsequent section. The suspension 210 was then heated to a temperature of about 680°C  
20 in preparation for casting. During this final heating, the suspension 210 was stirred by hand using the coated skimmer, which also served to intercept and remove from the suspension several small, undispersed pieces of the highly loaded metal matrix composite ingot material 204. Pairs of fluidity samples were additionally taken at temperatures of about 660°C and about 680°C,  
25 respectively. The suspension 210 was skimmed one final time and a portion of the suspension was then cast (Fig. 14d) into the preheated investment shell mold 110 using an investment shell cup 210 and a pair of ladles 114, 116 as depicted in Figure 15. The pouring technique shown in the Figure provided a smooth flow of molten composite material into the investment shell mold. A  
30 smooth flow of casting material is important to minimize turbulence-induced porosity in the solidified casting. Additionally, some of the investment shell gates contained filters comprising a reticulated ceramic material having about 10 openings per inch (3.9 openings per cm) as a further effort to prevent gross defects from entering the investment shell mold, particularly  
35 the tensile test specimen portion of the mold. The filled mold and its contents were subsequently allowed to cool.



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Once the investment shell mold 110 and its contents had cooled to about room temperature, the investment shell was removed with light hammer blows to reveal the cast metal matrix composite body contained within. The metal matrix composite body comprised the tensile test specimen and its attached gates and risers, as shown in Figure 17.

After the cast metal matrix composite was recovered from the investment shell mold, the tensile test specimens were removed from the attached gates and risers using a diamond saw and diamond machined according to the dimensional parameters and tolerances described in ASTM Method E8 for a gage diameter of about 0.31 inch (8 mm).

The machined tensile test specimens were then subjected to a T4 heat treatment. Specifically, the tensile test specimens were placed into a resistance heated air atmosphere furnace at a temperature of about 538°C. After exposing the tensile test specimens to a temperature of about 538°C for about 5 hours, the specimens were withdrawn from the furnace and quenched in approximately room temperature water.

A number of similar castings were made and the resulting cast metal matrix composite bodies were sectioned using a diamond saw and characterized according to the following techniques. The heat treatment, however, was performed only on those samples from which mechanical properties were to be measured.

#### Measurement of Ultimate Tensile Strength (U.T.S.)

The tensile strength was determined using ASTM Method E8, "Standard Test Methods for Tension Testing of Metallic Materials". The strain of the tension test specimen was measured with an extensometer designated 632.11B-20 from Material Testing Systems, Inc., of Minneapolis, MN. The tensile test specimen was placed into the gripping fixture on a 22,000 lb. (10,000 kg) load cell of a Model 810 servohydraulic fatigue testing machine (Material Testing Systems, Inc., Minneapolis, MN). A computer data acquisition system was connected to the measuring unit of the load cell and the extensometer to record the test responses. The test specimen was deformed at a constant rate of about 0.020 inches per minute (0.508 mm per minute) to failure. The ultimate tensile strength, the Young's modulus and the maximum strain (or total strain to failure) were calculated from the sample geometry and the recorded responses using programs within the computer. The proportional limit and the yield

strengths as measured at the 0.01% and 0.2% offset strains were computed using graphical methods.

#### Vacuum Fluidity Test

5           The fluidity of the molten contents of the bilge crucible was measured by noting the distance by which a vacuum could draw a portion of this melt or suspension up a tube before the melt froze within the tube. Specifically, a type 304 stainless steel tube measuring about 36 inches (914 mm) long and having an inside diameter of about 0.25 inch (6 mm) was connected at one end  
10       to a vacuum source of about 30 inches (762 mm) of mercury vacuum. The opposite end of the substantially room temperature tube was then immersed slightly under the surface of the test melt with the tube in a substantially vertical orientation. The vacuum drew a column of molten material a distance up the tube but the progress of the rising column of molten material was  
15       eventually halted by the solidification of the melt within the tube. The end of the tube was then withdrawn from the melt and the frozen column of test material was recovered from inside the tube and its length measured. The length of the recovered solidified material within the tube is proportional to the fluidity of the melt or suspension.

20

#### Quantitative Image Analysis

The samples of the present Example were image analyzed in substantially the same manner as were the materials of Example 1.

#### Sample B Material

25           A clean, dry STARRBIDE® 70 bilge crucible (American Refractories and Crucible Corp., North Haven, CT) having substantially the same dimensions as the crucible described earlier, was placed into a resistance heated air atmosphere furnace such that the lip of the crucible was substantially flush  
30       with the top surface of the furnace, and the furnace and its contents were heated to a temperature of about 800°C. Upon reaching a temperature of about 800°C, about 53 lbs. (24 kg) of DURALCAN™ metal matrix composite material which had been cleaned in ethanol, grit blasted and dried at a temperature of about 350°C in air for about 2 hours, was introduced into the crucible. The  
35       DURALCAN™ metal matrix composite material comprised by weight about 20% 39 CRYSTOLON® green silicon carbide particulate (Norton Co., Worcester, MA)

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having an average particle size of about 17 microns, and the balance a matrix metal comprising aluminum and about 10 weight percent silicon. An argon cover gas was introduced into the opening of the crucible at a flow rate of about 10 liters per minute. The opening at the top of the crucible was then covered  
5 with an approximately 2 inch (51 mm) thick layer of FIBERFRAX® ceramic fiber insulating material (Carborundum Company, Niagara Falls, NY). After about an hour and a half, the FIBERFRAX® blanket was removed from the top of the crucible to reveal that the DURALCAN™ metal matrix composite material had partially melted. At this time, an additional approximately 23 lbs. (10.5 kg)  
10 quantity of the DURALCAN™ metal matrix composite material was added to the crucible and the FIBERFRAX® blanket was replaced.

While the crucible and its contents were reheating to the set point temperature of about 800°C, an investment shell mold having a shape and composition substantially the same as that described earlier in this Example  
15 was prepared for the subsequent metal matrix composite casting operation by subjecting the investment shell mold to substantially the same thermal treatments as the previously described mold.

After heating the crucible and its contents for about an additional 3 hours, the FIBERFRAX® blanket was removed to reveal that the matrix metal of  
20 the metal matrix composite material in the crucible had substantially completely melted. Accordingly, this metal matrix composite suspension was manually stirred at intervals of about 10 minutes using the ZIRCWASH® coated skimmer described previously. After about an additional hour, the temperature of the metal matrix composite suspension was reported to be about 685°C. The  
25 periodic stirring was continued. After about an additional hour and a quarter, the temperature of the DURALCAN™ metal matrix composite suspension was reported to be about 722°C. A pair of fluidity samples were taken at this temperature, as the suspension was ready for casting.

The DURALCAN™ metal matrix composite suspension was then cast into the  
30 approximately 540°C preheated investment shell mold in substantially the same manner as was described previously and was illustrated in Figure 16. As in the case of the casting described previously, some of the gates in the investment shell contained metal filters comprising the aforementioned reticulated ceramic material, and other gates contained no such filters.

After the investment shell mold had been substantially completely filled with the DURALCAN™ metal matrix composite suspension, the mold and its contents were allowed to cool back to room temperature.

Once the investment shell mold and its contents had cooled to about room temperature, the investment shell was removed with light hammer blows to reveal the cast metal matrix composite body, and the cast metal matrix composite body was sectioned, machined, heat treated and characterized in substantially the same manner as was the cast metal matrix composite body described previously. Again, only the mechanical property test samples were heat treated.

The following paragraphs describe the comparison of certain characteristics of each cast metal matrix composite based upon the characterizations discussed previously.

Figure 18 shows melt fluidity as measured in the vacuum fluidity test as a function of melt temperature. The data points represented by the open triangles represent Sample A metal matrix composite suspension material containing the 39 CRYSTOLON® Strong (Rounded) green silicon carbide filler), the shaded squares represent Sample B metal matrix composite suspension material (containing the 39 CRYSTOLON® silicon carbide filler) and the shaded diamonds represent molten aluminum-10 silicon unreinforced matrix metal. Figure 18 clearly shows that the fluidity of each of the metal matrix composite suspensions is less than that of the molten, unreinforced matrix metal, and also suggests that, at a given temperature, the Sample A material is at least somewhat more fluid than the molten Sample B metal matrix composite material.

Table III reports mechanical property test data which was measured at about room temperature on 10 and 12 tensile test specimens, respectively, of the Sample A and Sample B cast metal matrix composite materials, respectively. The effect of the presence or absence of a filter in the investment shell mold during casting of the molten metal matrix composite material was not taken into consideration in the statistical analysis of the data, but the test data represents both filtered and unfiltered types of castings. The Table shows that the Sample A cast metal matrix composite material has a higher ultimate tensile strength, Young's modulus, proportional limit and yield strength than the corresponding Sample B cast metal matrix composite material. The average strain to failure of the Sample A cast metal matrix composite material was

lower than that of the Sample B cast metal matrix composite material. With the exception, perhaps, of the proportional limit, the differences may not be statistically significant.

Table III  
Property Comparison of Cast Metal Matrix Composites

	<u>Sample A</u>	<u>Sample B</u>
Ultimate Tensile Strength (MPa)	272 $\pm$ 22	252 $\pm$ 15
Young's Modulus (GPa)	104 $\pm$ 7	100 $\pm$ 2
Proportional Limit (MPa)	101 $\pm$ 8	80 $\pm$ 4
Yield Strength (MPa)		
@ 0.01% offset	134 $\pm$ 10	125 $\pm$ 4
@ 0.2% offset	231 $\pm$ 15	214 $\pm$ 6
Strain-to-Failure (%)	0.78 $\pm$ 0.14	0.83 $\pm$ 0.17

Values reported are the arithmetic averages plus or minus one standard deviation.

The composite of the Sample A cast metal matrix composite material as measured by quantitative image analysis comprised by volume about 0.5% porosity, about 21.7% silicon carbide and the balance matrix metal.

The corresponding composition of the Sample B cast metal matrix composite material also as measured by quantitative image analysis comprised by volume about 0.6% porosity, about 18.8% silicon carbide and the balance matrix metal.

Figure 19 is an optical photomicrograph of a polished cross-section of the Sample A cast metal matrix composite material taken at approximately 1000X magnification which shows the silicon carbide filler material 130, aluminum matrix metal 132 and primary silicon precipitates 134 contained therein.

Figure 20 is an approximately 1000X magnification optical photomicrograph of the Sample B cast metal matrix composite material showing the silicon carbide filler material 140, the aluminum matrix metal 142 and primary silicon precipitates 144.

The composition of the Sample A cast metal matrix composite material was selected so as to be similar to the composition of the commercially available

Sample B cast metal matrix composite material. Specifically, the matrix metals have substantially the same composition and the filler materials are of substantially the same chemical composition and comprise approximately the same volume fraction of the overall metal matrix composite. The optical photomicrographs of Figures 19 and 20, however, reveal at least two apparent differences between these two materials. First, the Sample A material comprises a filler material having a more rounded morphology, whereas that of the Sample B material is more blocky and contains more acute angles. Furthermore, the silicon precipitates in the matrix metal of the Sample A material appear to be larger in size than the corresponding precipitates of the Sample B material.

In terms of properties or characteristics of the two cast metal matrix composite materials, the Sample A material shows a slightly greater fluidity for a given temperature than the Sample B material. Additionally, although potentially not statistically significant, the Sample A material also appears to show slightly superior mechanical properties compared to those of Sample B. Moreover, it may be possible to improve the mechanical properties of the Sample A material by reducing the size of the primary silicon precipitates to a size similar to those observed in the Sample B material.

### Example 3

The following Example demonstrates, among other things, some mechanical properties of metal matrix composite bodies formed either by the spontaneous infiltration of a matrix metal into a strong filler material or by the subsequent dilution of the metal matrix composite body formed by a spontaneous infiltration technique with additional matrix metal. Specifically, the corrected flexural strengths of metal matrix composite bodies as a function of test temperature are reported. More specifically, the corrected flexural strengths of metal matrix composite bodies comprising a strong filler material with varying particle size distributions or a standard filler material with varying particle size distributions are compared to the corrected flexural strength of the matrix metal alloy. Table IV sets forth the filler material and size, the matrix metal composition, the processing temperature, processing time and volume percent filler for Samples C-G of this Example.

TABLE IV

<u>Sample</u>	<u>Filler Material and Size</u>	<u>Matrix Metal</u>	<u>Processing Temperature</u>	<u>Processing Time</u>	<u>Volume Percent Filler</u>
C	500 grit strong (rounded) green silicon carbide	Al-10 wt% silicon	Substantially as Sample A of Example 2		30
D	500 grit strong (rounded) green silicon carbide	Al-12 wt% silicon	785°C	12 hours	61
E	80 wt% 220 grit and 20 wt% 500 grit regular silicon carbide	AA 336.0 alloy#	780°C	1.5 hours	58
F	500 grit strong (rounded) green silicon carbide	AA 336.0 alloy#	780°C	4 hours	57
G	800 grit strong (rounded) green silicon carbide	AA 336.0 alloy#	780°C	12 hours	47

NOTE: All filler materials were obtained from Norton Co., Worcester, MA.

#Nominal Composition: 11.0-13.0 wt% silicon,  $\leq 1.2$  wt% iron, 0.5-1.5 wt% copper,  $\leq 0.35$  wt% manganese, 0.8-1.3 wt% magnesium, 2.0-3.0 wt% nickel,  $\leq 0.35$  wt% zinc,  $\leq 0.25$  wt% titanium and the balance aluminum.

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Sample C

Sample C was made substantially in accordance with the methods of Sample A of Example 2. Specifically, Sample C comprised a 39 CRYSTOLON® 500 grit (average particle diameter of about 15.6 microns) strong (rounded) green silicon carbide reinforced aluminum metal matrix composite body. The matrix metal of Sample C comprised an aluminum 10 weight percent silicon alloy. The filler loading for Sample C was about 30 volume percent.

Samples D, F and G

Samples D, F and G were made substantially in accordance with the methods of Example 1, except for the differences in filler material size, matrix metal, processing temperature and processing time as noted in Table IV. Specifically, Sample D comprised a 39 CRYSTOLON® 500 grit (average particle diameter of about 15.6 microns) strong (rounded) green silicon carbide (Norton Co., Worcester, MA) reinforced metal matrix composite body. The matrix metal for Sample D comprised an aluminum 12 weight percent silicon alloy. The volume percent filler loading for Sample D was about 61%. Sample F comprised a 39 CRYSTOLON® 500 grit (average particle diameter of about 15.6 microns) strong (rounded) green silicon carbide (Norton Co., Worcester, MA) reinforced metal matrix composite body. The matrix metal for Sample F comprised an AA 336.0 alloy (having a nominal composition by weight of about 11.0-13.0% silicon,  $\leq 1.2\%$  iron, 0.5-1.5% copper,  $\leq 0.35\%$  manganese, 0.8-1.3% magnesium, 2.0-3.0% nickel,  $\leq 0.35\%$  zinc,  $\leq 0.25\%$  titanium and the balance aluminum). The volume percent filler loading for Sample F was about 57%. Sample G comprised a 39 CRYSTOLON® 800 grit (average particle diameter of about 8.3 microns) strong (rounded) green silicon carbide (Norton Co., Worcester, MA) reinforced metal matrix composite body. The matrix metal for Sample G comprised an AA 336.0 alloy. The volume percent filler for Sample G was about 47%.

Sample E

Sample E was produced by the methods described below. Specifically, a graphite boat having inner cavity dimensions measuring about 5 inches (127 mm) square and about 2.5 inches (64 mm) high and having a wall thickness of about 0.28 inch (7.1 mm) was used. The graphite boat was machined from Grade ATJ graphite (Union Carbide Corp., Carbon Products Division, Cleveland, OH). The inner surface of the graphite boat was spray coated with a colloidal graphite mixture comprising about 1 part by volume ethanol (Pharmco Products, Inc.,



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Bayone, NJ) and about 1 part by volume of a DAG® 154 colloidal graphite (Acheson Colloids, Port Huron, MI). At least 3 spray coats of the colloidal graphite mixture were applied to the inner surface of the graphite boat using an air brush. Each coat of the colloidal graphite mixture was permitted to dry before a subsequent coat was applied. The coated graphite boat was placed into a resistance heated air atmosphere furnace set at about 380°C for about 2 hours to harden the colloidal graphite coating. The graphite boat with the hardened colloidal graphite coating, after being removed from the furnace, was exposed to an air atmosphere at about room temperature for about 2 hours. The colloidal graphite coated boat was then stored in a vacuum oven set at about 150°C for about 12 hours.

A silicon carbide reinforcement material mixture comprising by weight about 20 percent 39 CRYSTOLON® 500 grit (average particle diameter of about 17 microns) regular silicon carbide and about 80 percent 39 CRYSTOLON® 220 grit (average particle diameter of about 66 microns) regular silicon carbide (both from Norton Co., Worcester, MA) was blended until substantially homogeneous. The reinforcement material mixture was placed onto a steel tray which was subsequently placed into a vacuum oven. The vacuum oven was set at about 150°C and evacuated to about 30 inches (762 mm) of mercury. After about 12 hours, the silicon reinforcement material mixture was removed from the vacuum oven and allowed to cool in an air atmosphere at about room temperature for about 1 hour.

A filler material mixture was made by adding about 3% by weight -325 mesh (particle diameter less than about 45 microns) magnesium powder (Reade Manufacturing Co., Lakehurst, NJ) to the reinforcement material mixture within a NALGENE® plastic jar (Nalge Co., Rochester, NY). The plastic jar and its contents were roll milled for about 30 minutes to form a filler material mixture.

The colloidal graphite coated graphite boat, which had been stored in a vacuum oven for about 12 hours, was removed from the vacuum oven and about 700 grams of the filler material mixture comprising the silicon carbide reinforcement mixture and the magnesium, were poured into the bottom of the colloidal graphite coated graphite boat. The bottom of the graphite boat was then tapped several times on a table top to level the surface of the filler material mixture. The leveled surface of the filler material mixture was then coated with about 1 gram of -50 mesh (particle diameter less than about 300

microns) magnesium powder (Alpha Products, Morton Thiokol, Danvers, MA).

About 1170 grams of matrix metal ingots, comprising an AA 336.0 alloy (having a nominal composition by weight of about 11.0-13.0% silicon,  $\leq 1.2\%$  iron, 0.5-1.5% copper,  $\leq 0.35\%$  manganese, 0.8-1.3% magnesium, 2.0-3.0% nickel,  $\leq 0.35\%$  zinc,  $\leq 0.25\%$  titanium and the balance aluminum) were placed on the filler material mixture coated with the magnesium powder. The colloidal graphite coated boat and its contents were placed into a stainless steel container measuring about 10 inches (254 mm) long, about 12 inches (305 mm) wide and about 10 inches (254 mm) high. The bottom of the stainless steel container had been prepared by covering the bottom of the container with a piece of PERMA-FOIL™ graphite foil (TTAmerica, Portland, OR) measuring about 10 inches (254 mm) long, about 12 inches (305 mm) wide and about 0.01 inch (0.25 mm) thick. A firebrick was placed on the graphite foil to support the colloidal graphite coated graphite boat within the stainless steel container. About 15 grams of a titanium sponge material (Chemalloy Co., Inc., Bryn Mawr, PA) and about 4 grams of -50 mesh (particle diameter less than about 300 microns) magnesium (Alpha Products, Morton Thiokol, Danvers, MA) were sprinkled onto the graphite foil in the bottom of the stainless steel container and around the firebrick. A sheet of copper foil was placed over the opening of the stainless steel container to form an isolated chamber, and a nitrogen purge tube was provided through the side of the stainless steel container to complete a lay-up.

The lay-up comprising the stainless steel container and its contents was placed into a resistance heated air atmosphere furnace. The furnace and its contents were heated from about room temperature to about 600°C at a rate of about 400°C per hour while nitrogen gas flowed through the lay-up at a flow rate of about 10 liters per minute, then from about 600°C to about 780°C at a rate of about 400°C per hour while nitrogen gas flowed through the lay-up at a flow rate of about 2 liters per minute. The furnace and its contents were maintained at about 780°C for about 1.5 hours while nitrogen gas flowed through the lay-up at a flow rate of about 2 liters per minute. The lay-up comprising the stainless steel container and its contents was then removed from the furnace and the graphite coated graphite boat was removed from the stainless steel container and placed onto a room temperature water cooled copper chill plate to directionally solidify the matrix metal of the formed metal matrix composite body.

Flexural Strength Measurements at Room and Elevated Temperature

Metal matrix composite bodies designated Samples C-G, as well as an AA 336.0 alloy, were prepared for flexural strength measurement as a function of temperature. Specifically, the metal matrix composite bodies and the matrix metal were sectioned with a diamond blade into specimens measuring about 0.12 inch (3 mm) thick, about 0.25 inch (6 mm) wide and about 2.6 inches (66 mm) long. The flexural strength of the metal matrix composite bodies and the AA 336.0 alloy were determined using a four-point bend test substantially the same as military standard (MIL-STD-1942-A) at temperatures of about 22, 100, 200, 300, 400, 450 and 500°C. The flexural strengths were determined by placing the specimens on a lower span of a four-point bend apparatus. The lower span measured about 1.6 inches (40 mm). The upper span measured about 0.8 inch (20 mm) and was brought into contact with the specimen to be tested. A constant displacement of about 0.02 inch (0.5 mm) per minute was exerted upon each specimen until the specimen failed. Flexural strengths measured at about 22°C were performed with a Model CITS-20006 Universal Testing Machine (System Integration Technology, Inc., Stratton, MA) equipped with a Model 3132-149, about 5,000 pound (2,282 kg) load cell (Eaton Corp., Troy, MI). Flexural strengths measured at about 100, 200, 300, 400, 450 and 500°C were performed using a Model CITS-2000-6W Universal Testing Machine (System Integration Technology, Inc., Stratton, MA) equipped with a Model 3132-149, about 500 pound (228 kg) load cell (Eaton Corp., Troy, MI) and a Series 3350 resistance heated air atmosphere furnace (Applied Systems, Inc., Butler, PA). The specimens that were used to determine the flexural strength of the metal matrix composite bodies and the matrix metal at elevated temperatures were held at the test temperature for at least 1 hour. Additionally, the temperature of one of the specimens for each series of tests at a given temperature was monitored using a Type K thermocouple at least within 0.31 inch (10 mm) of the specimen. The data for each test was collected using a data acquisition system interfaced with a computer. The results of the flexural strength tests were plotted as load as a function of displacement. In addition, the cross-sectional dimensions of each specimen was noted prior to performing the tests. To convert the strength results of the four-point flexural strength test to tensile strength, a method described in "Theory of Flow and Fracture of Solids" by A. Nadai, Volume 1, Second Edition, published

by MacGraw Hill Book Co., Inc., New York, NY, 1950, in Chapter 22 on pages 353-359, was used. Specifically, this method assumes that the tensile and compression stress strain curves of the material are substantially the same.

Figure 21 is a graph of the corrected flexural strength (i.e., tensile strength) as a function of test temperature of metal matrix composite bodies designated Samples C (designated "Curve C" on Figure 21) and D (designated "Curve D" on Figure 21), as well as matrix AA 336.0 alloy (designated "Curve B" on Figure 21) as a function of temperature. Additionally, Figure 21 contains an estimate of the corrected flexural strength of an unreinforced matrix alloy (designated "Curve A" on Figure 21) corresponding substantially in composition to the matrix metal of Samples C and D. Figure 21 illustrates that the corrected flexural strength as a function of temperature increases with the increased volume percent filler loading in a metal matrix composite body.

Figure 22 is a graph showing the corrected flexural (i.e., tensile strength) strength of metal matrix composite bodies designated Samples E (designated "Curve E" on Figure 22), F (designated "Curve F" on Figure 22) and G (designated "Curve G" on Figure 22), as well as matrix AA 336.0 alloy (designated "Curve B" on Figure 22) as a function of temperature. Figure 22 suggests that the corrected flexural strength as a function of temperature is affected by the particle size of the reinforcement filler material reinforcing the matrix metal. Specifically, Figure 22 suggests that as the particle size of the reinforcement filler material decreases, the corrected flexural strength of the resultant composite body increases.

Figure 23 is a photomicrograph taken at a magnification of about 400X corresponding to Sample C. In addition, the results of quantitative image analysis performed substantially in accordance to the method of Example 1 analyzing an area measuring about 0.0053 square inch (3.44 square millimeters) at a magnification of about 500X showed that the metal matrix composite body was comprised by volume of about 30.6% 500 grit strong (rounded) green silicon carbide, about 0.8% pores and about 68.6% matrix metal.

Figure 24 is a photomicrograph taken at a magnification of about 400X corresponding to Sample D. In addition, the results of quantitative image analysis performed substantially in accordance to the method of Example 1 analyzing an area measuring about 0.005 square inch (3.23 square millimeters) at a magnification of about 500X showed that the metal matrix composite body

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was comprised by volume of about 61% 500 grit strong (rounded) green silicon carbide, about 3% pores and about 36% matrix metal.

Figure 25 is a photomicrograph taken at a magnification of about 400X corresponding to Sample F. In addition, the results of quantitative image analysis performed substantially in accordance to the method of Example 1 analyzing an area measuring about 0.005 square inch (3.23 square millimeters) at a magnification of about 500X showed that the metal matrix composite body was comprised by volume of about 57% 500 grit strong (rounded) green silicon carbide, about 2% pores and about 41% matrix metal.

Figure 26 is a photomicrograph taken at a magnification of about 400X corresponding to Sample G. In addition, the results of quantitative image analysis performed substantially in accordance to the method of Example 1 analyzing an area measuring about 0.0057 square inch (3.68 square millimeters) at a magnification of about 500X showed that the metal matrix composite body was comprised by volume of about 47% 800 grit strong (rounded) green silicon carbide, about 1% pores and about 52% matrix metal.

Thus, this Example demonstrates the corrected flexural strength (i.e., tensile strength) of strong (rounded) green silicon carbide reinforced metal matrix composite bodies as a function of temperature. Additionally, this Example demonstrates that as the volume percent filler loading is increased, the resultant corrected flexural strength of the metal matrix composite body increases and that as the particle size of the reinforcement material is decreased, the corrected flexural strength of the resultant metal matrix composite body increases.

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What is Claimed is:

1. A metal matrix composite comprising:  
a matrix metal; and  
a filler material at least partially embedded by said matrix metal, said  
5 filler material exhibiting a morphology which enhances at least one property  
of said metal matrix composite body.
2. A metal matrix composite body comprising:  
an aluminum matrix metal; and  
10 a 39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate  
manufactured by the Norton Company, at least partially embedded by said  
aluminum matrix metal.
3. The metal matrix composite body of claim 2, wherein said silicon  
15 carbide particulate has a particle size of about 500 grit.
4. The metal matrix composite body of claim 2, wherein said silicon  
carbide particulate has a particle size of about 800 grit.
- 20 5. A method for making a metal matrix composite body comprising:  
providing a filler material which exhibits a morphology which enhances  
at least one property of a formed metal matrix composite body; and  
providing a matrix metal such that said matrix metal at least partially  
embeds said filler.
- 25 6. The method of claim 5, wherein said filler material comprises a  
39 CRYSTOLON® Strong (Rounded) green silicon carbide particulate manufactured  
by the Norton Company.
- 30 7. The method of claim 6, wherein said matrix metal comprises aluminum.
8. The method of claim 5, wherein said matrix metal at least partially  
embeds said filler due to a spontaneous infiltration process.
- 35 9. A metal matrix composite comprising:  
a matrix metal; and

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a filler material at least partially embedded by said matrix metal, said filler material exhibiting features depicted in Figures 5, 6, 7 and 8.

10. A metal matrix composite body comprising:

an aluminum matrix metal; and

a silicon carbide particulate filler material at least partially embedded by said aluminum matrix metal, said silicon carbide particulate filler material exhibiting features as depicted in Figures 5, 6, 7 and 8.

11. The metal matrix composite body of claim 10, wherein said silicon carbide particulate has a particle size of about 500 grit.

12. The metal matrix composite body of claim 10, wherein said silicon carbide particulate has a particle size of about 800 grit.

13. The metal matrix composite of claim 9, wherein said matrix metal comprises at least one matrix metal selected from the group of matrix metals consisting of aluminum, magnesium, silicon, titanium, copper, bronze, cast iron, hafnium and combinations thereof.

14. The metal matrix composite of claim 9, wherein said filler material comprises at least one filler material selected from the group of filler materials consisting of oxides, carbides, borides, nitrides, and mixtures thereof.

15. The metal matrix composite body of claim 9, wherein said matrix metal comprises aluminum and said filler material comprises at least one filler material selected from the group consisting of oxides, carbides, borides, nitrides and mixtures thereof.

16. The metal matrix composite of claim 9, wherein said matrix metal comprises aluminum and said filler material comprises at least one filler material selected from the group consisting of alumina, magnesia, zirconia, silicon carbide, aluminum dodecaboride, titanium diboride, aluminum nitride, silicon nitride and mixtures thereof.

17. The metal matrix composite body of claim 11, wherein said silicon carbide particulate, prior to incorporation in the composite body, has a tap density of about 1.9 grams per cubic square centimeter.

5

18. The metal matrix composite body of claim 11, wherein said silicon carbide particulate, prior to incorporation into said composite body, has a surface area of about 0.76 square meters per gram.

10

19. The metal matrix composite body of claim 12, wherein said silicon carbide particulate, prior to incorporation in said composite body, has a tap density of about 1.7 grams per cubic centimeter.

15

20. The metal matrix composite body of claim 16, having an ultimate tensile strength measured at about room temperature by ASTM Method E8 of at least 272 MPa.

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21. The metal matrix composite of claim 13, wherein said filler material comprises at least one filler material selected from the group of filler materials consisting of oxides, carbides, borides, nitrides, and mixtures thereof.



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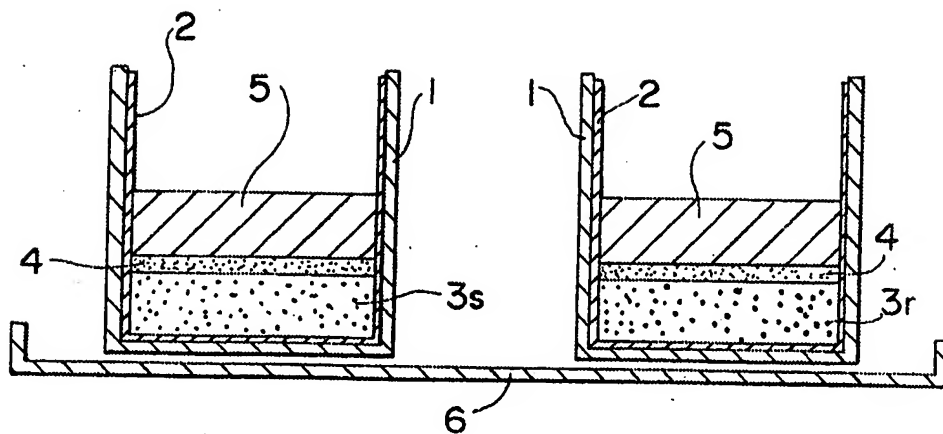


Fig. 1

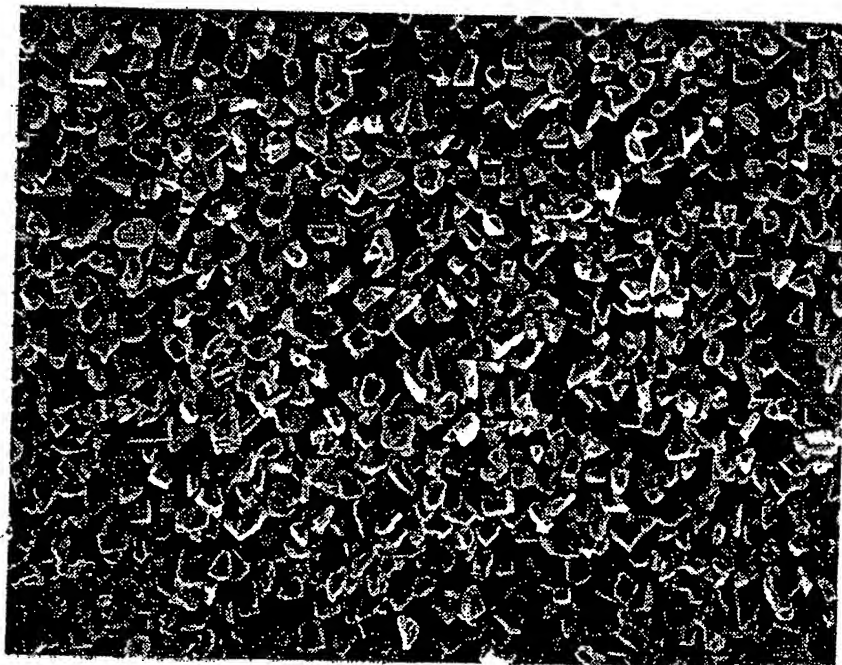


Fig. 2

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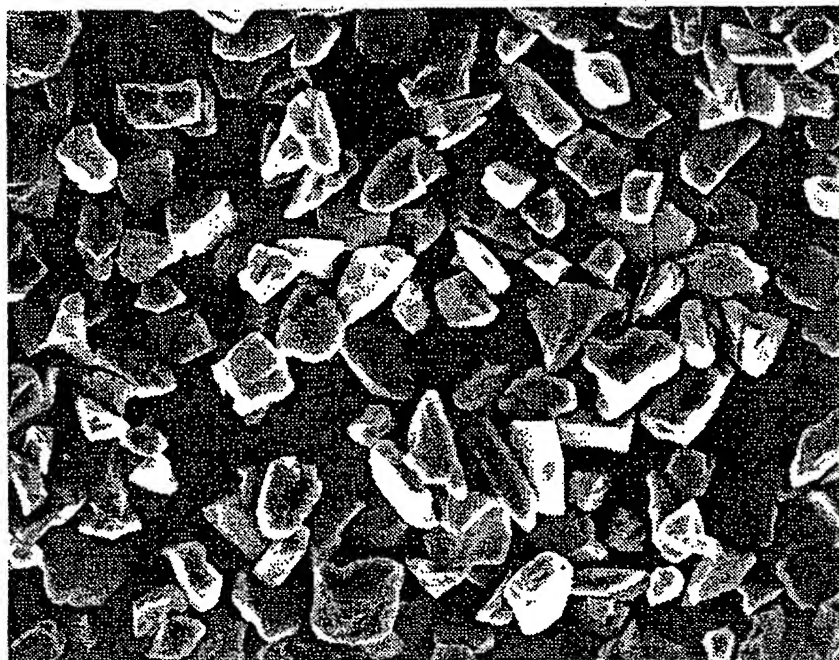
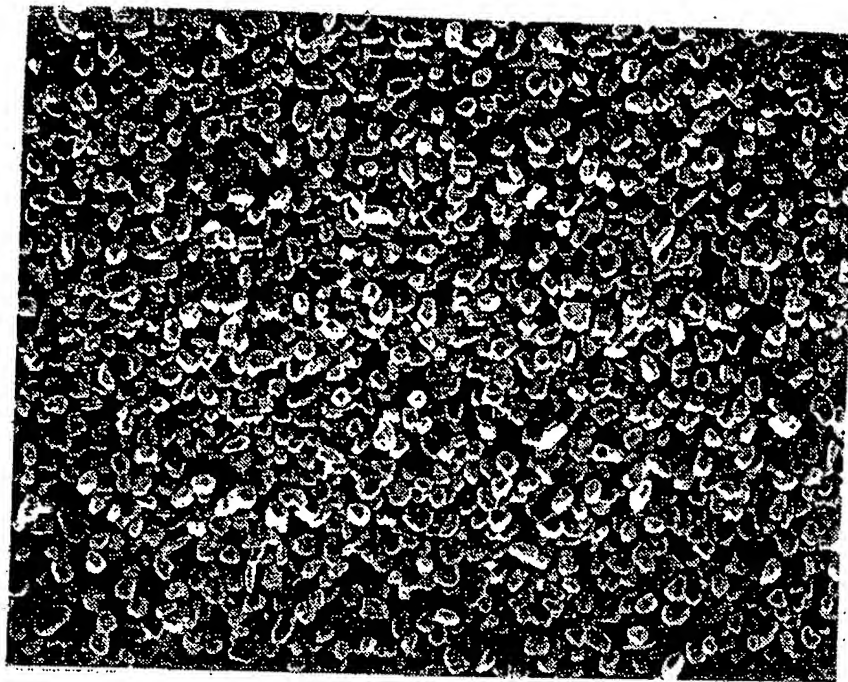


Fig. 3

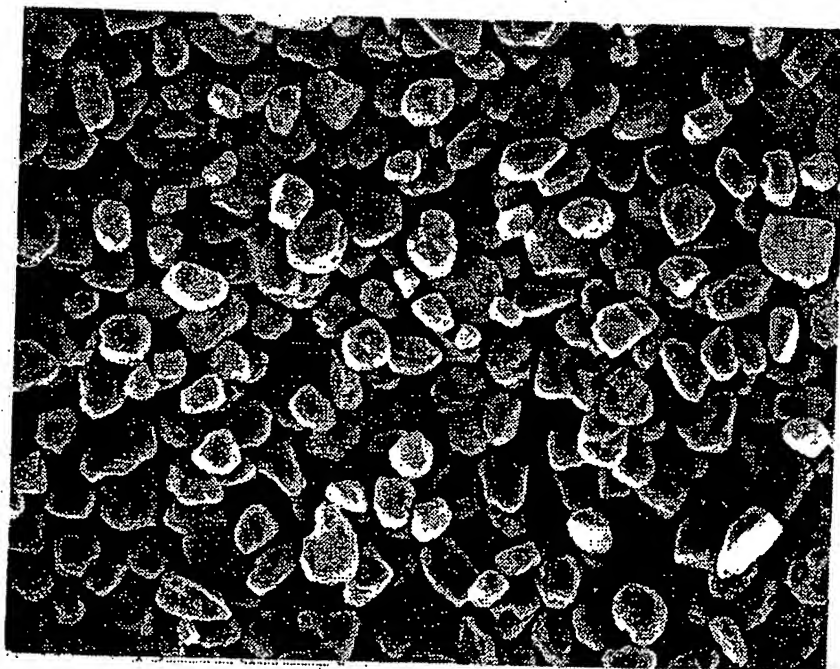


Fig. 4

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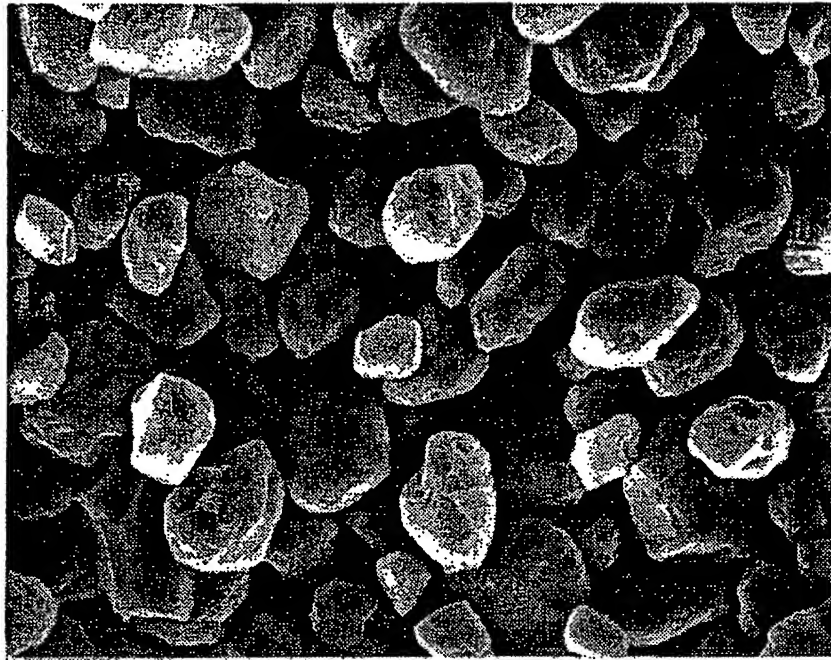


**Fig. 5**



**Fig. 6**

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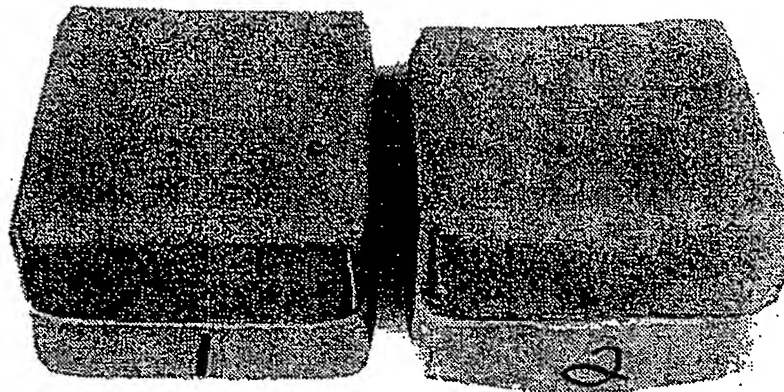


**Fig. 7**

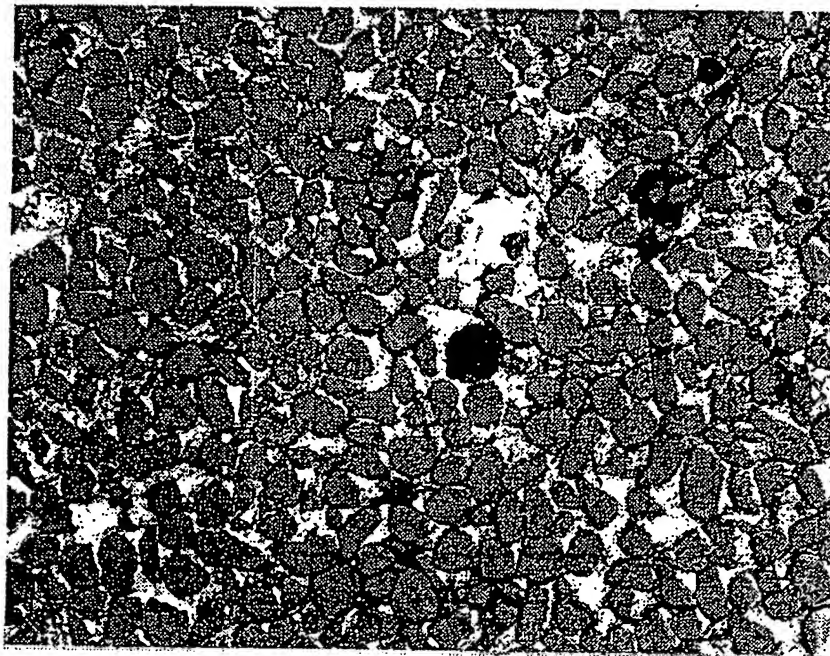


**Fig. 8**

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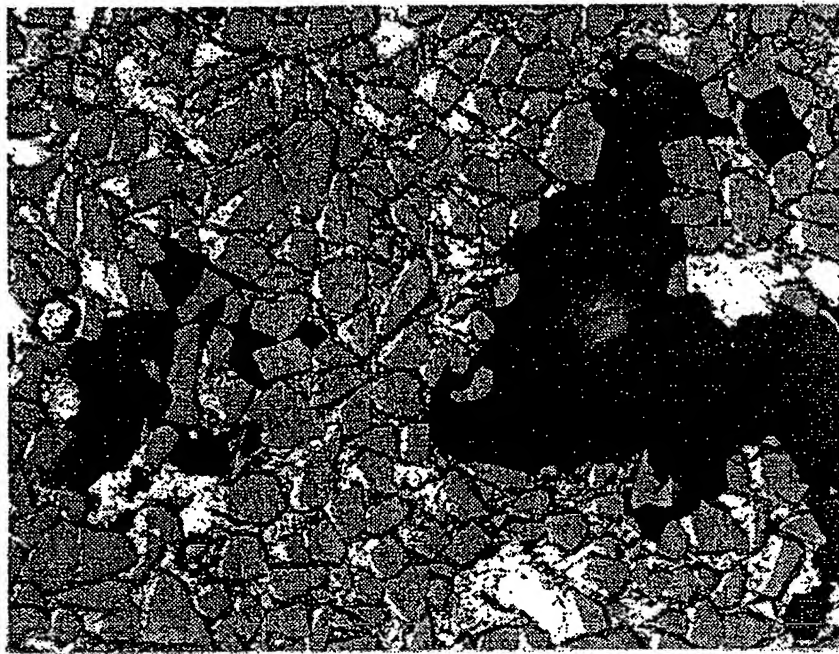
**Fig. 9**



**Fig. 10**

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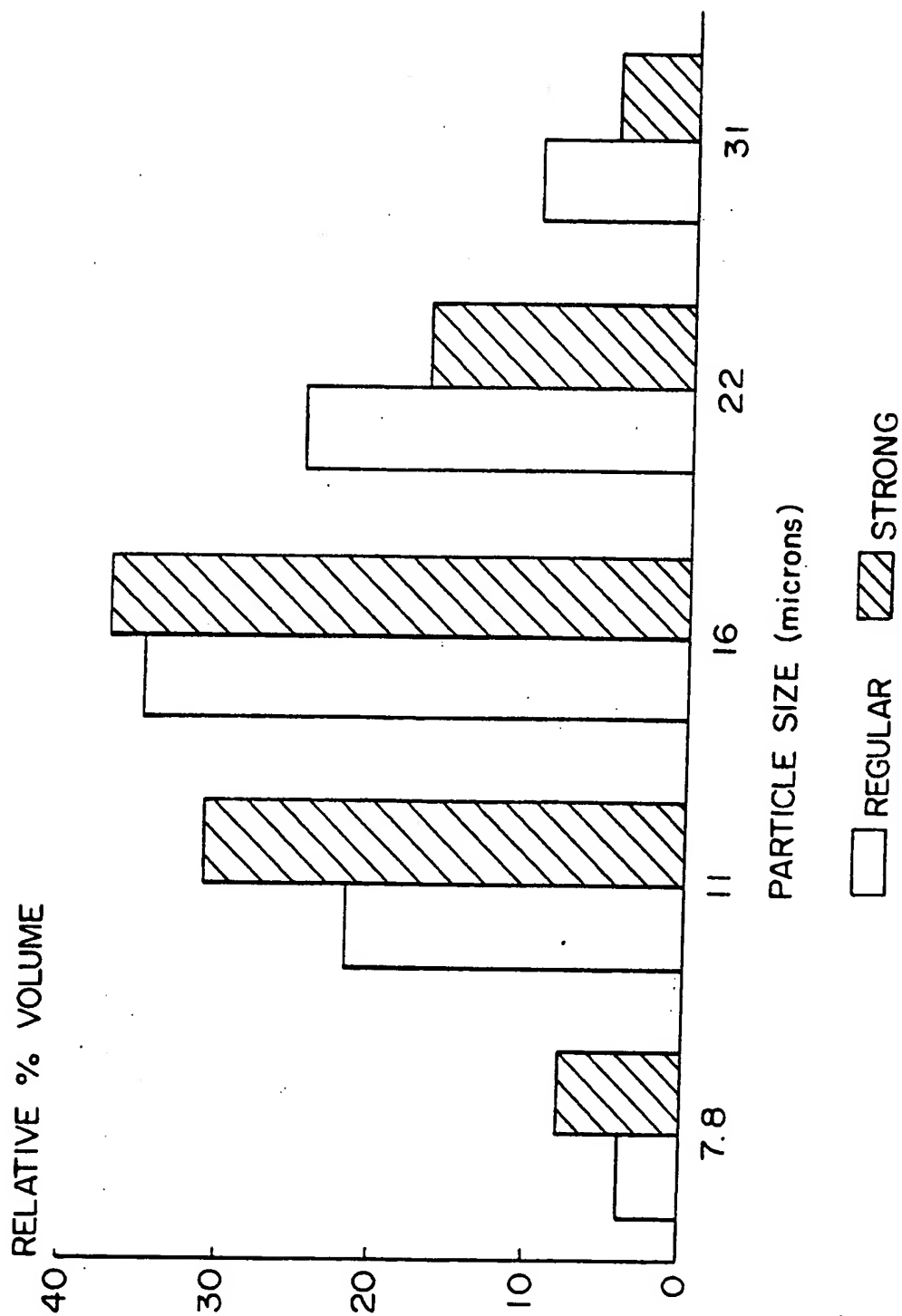


**Fig. II**

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Fig. 12



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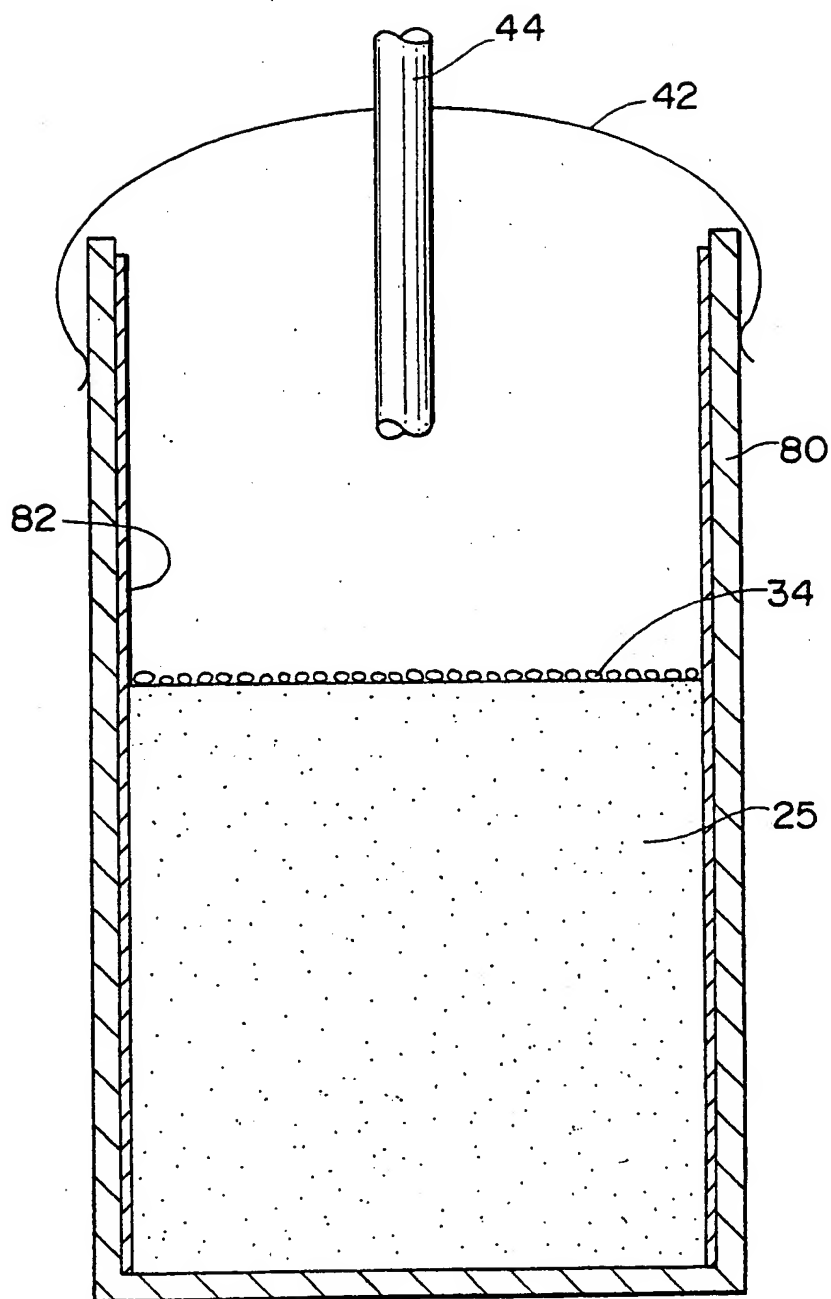


Fig. 13



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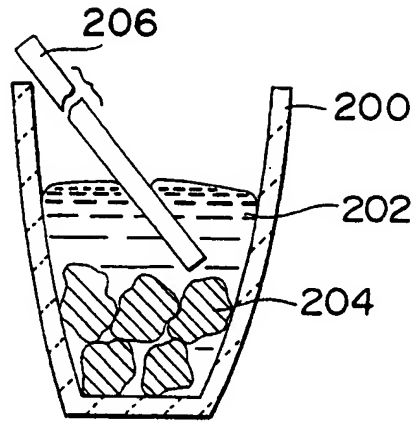


Fig. 14a

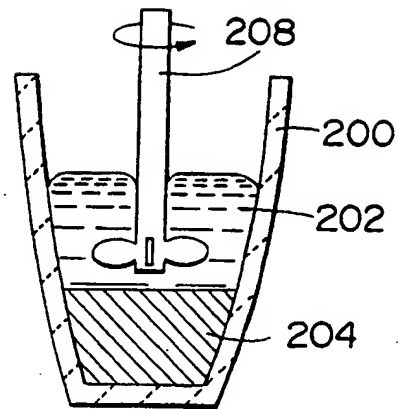


Fig. 14b

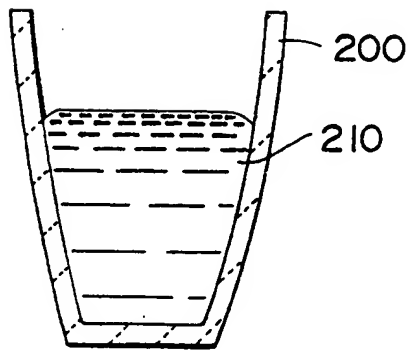


Fig. 14c

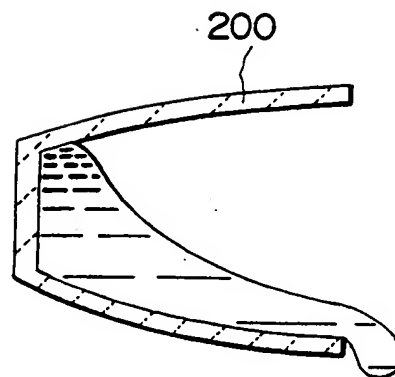
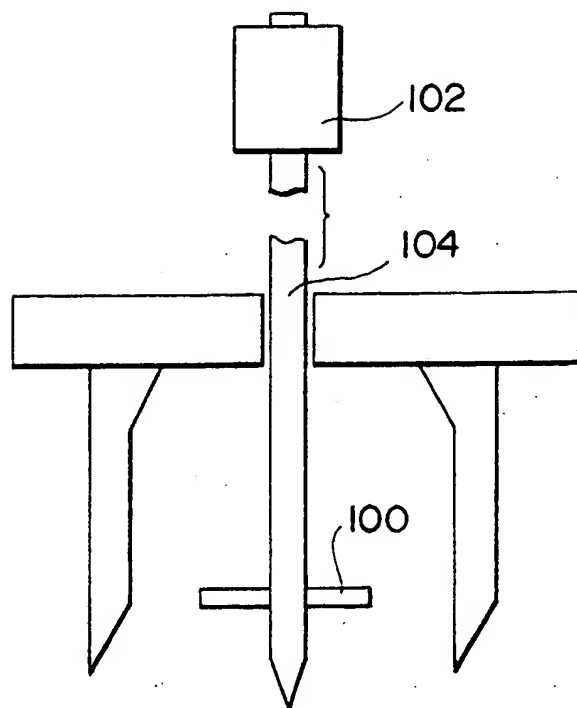
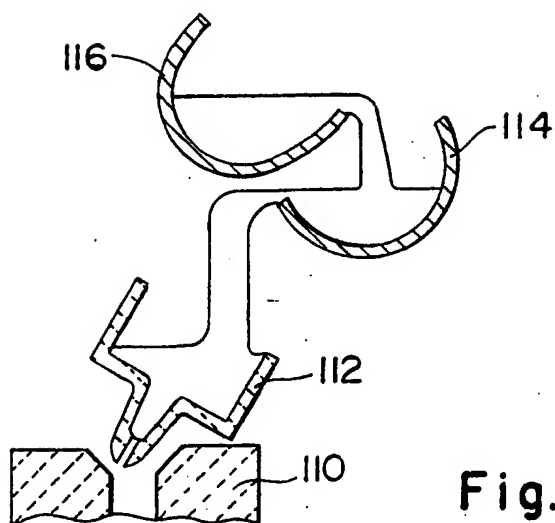


Fig. 14d

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**Fig. 15**



**Fig. 16**

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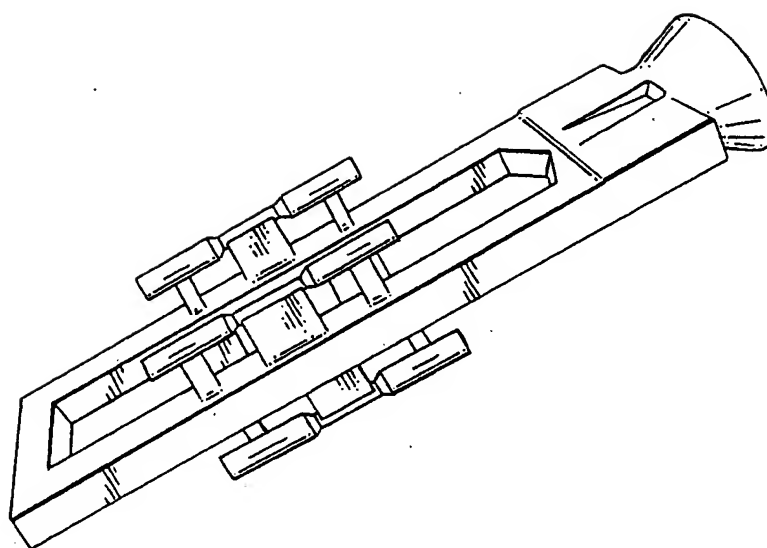
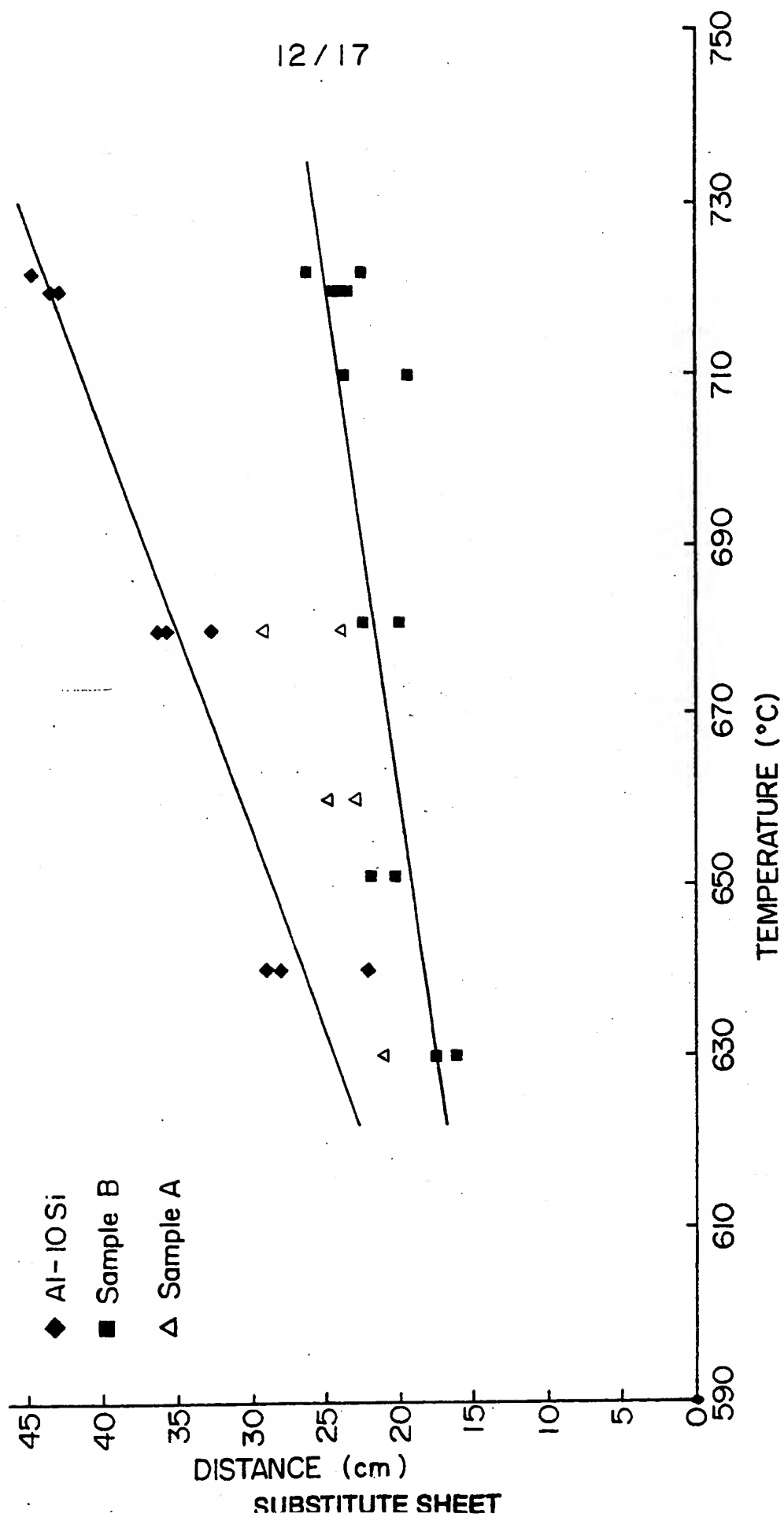


Fig. 17

Fig. 18



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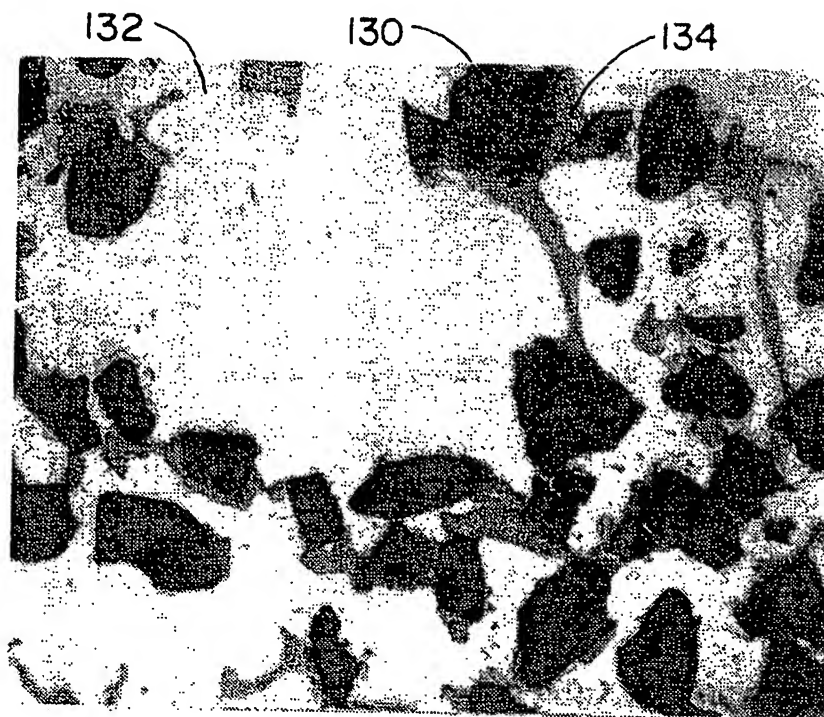


Fig. 19

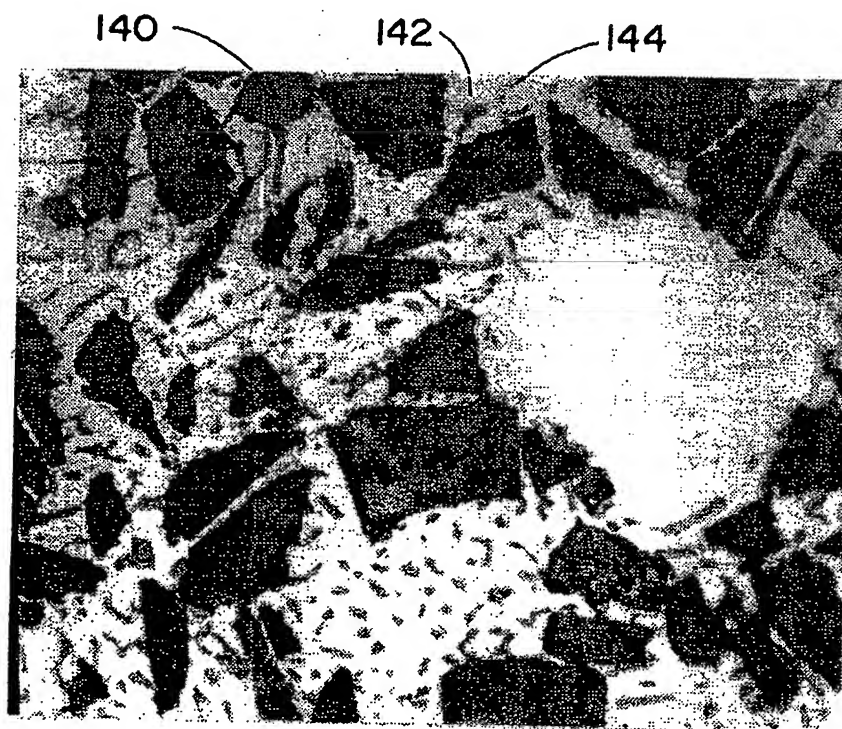
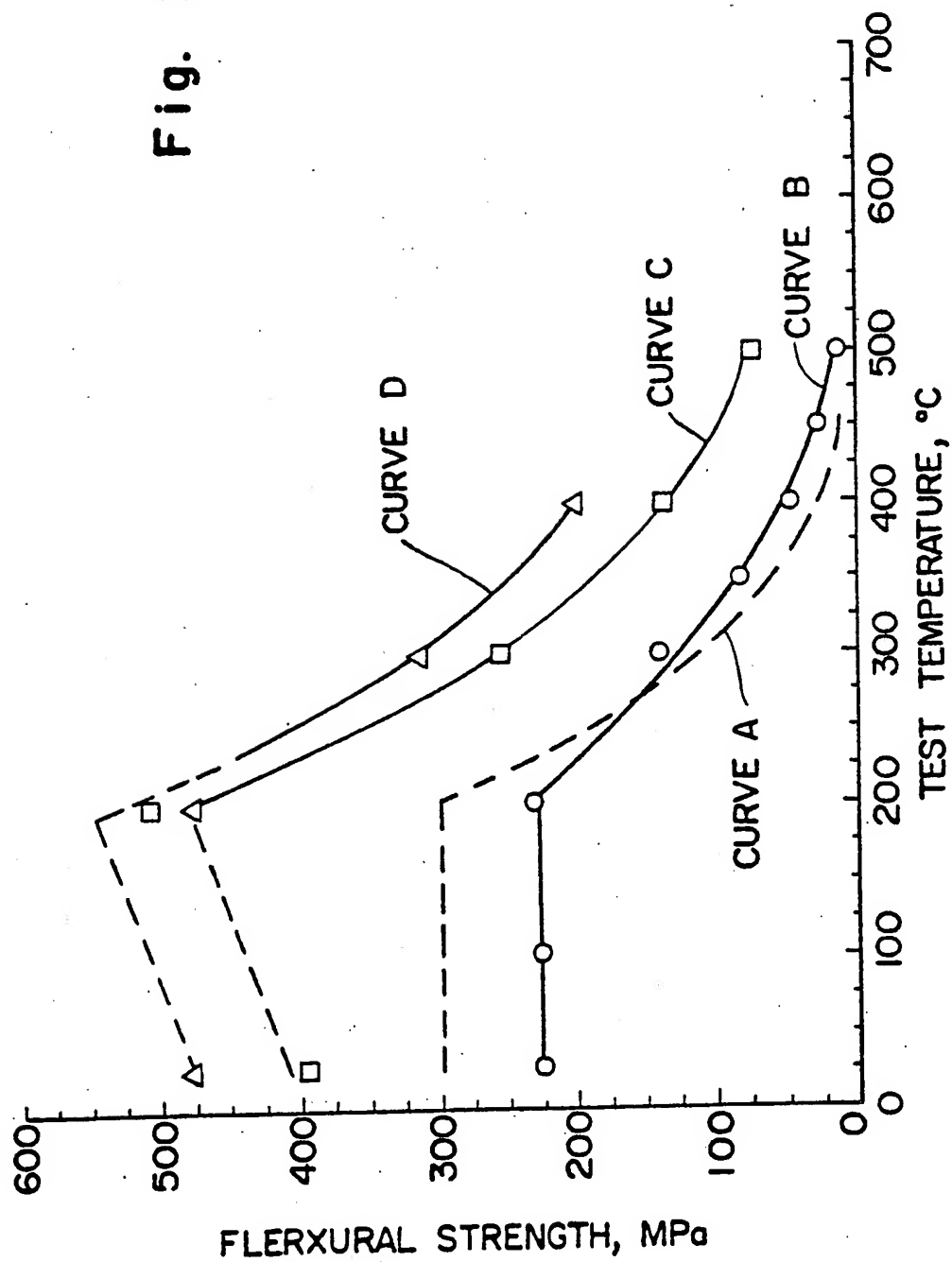


Fig. 20

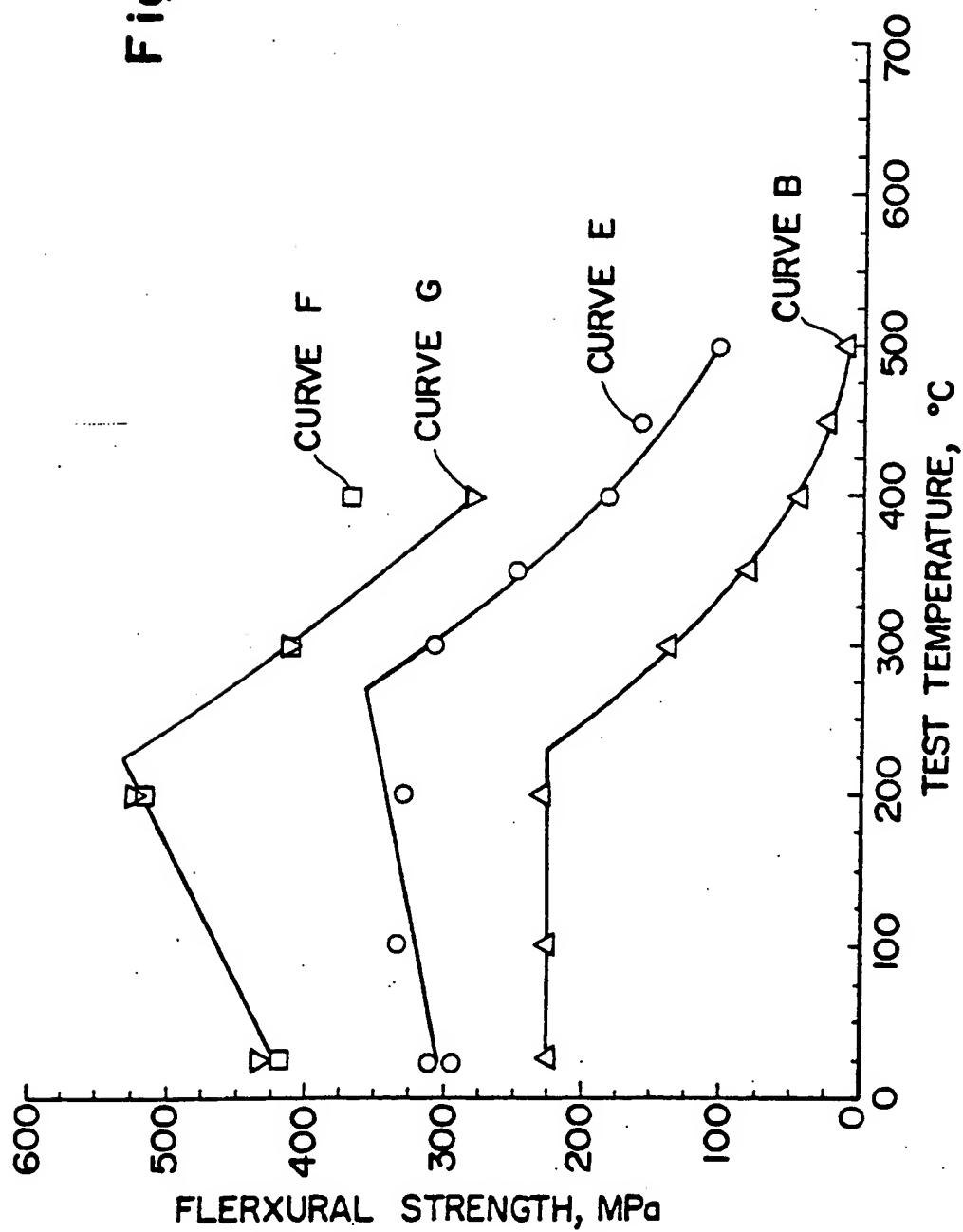
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Fig. 21



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Fig. 22



SUBSTITUTE SHEET

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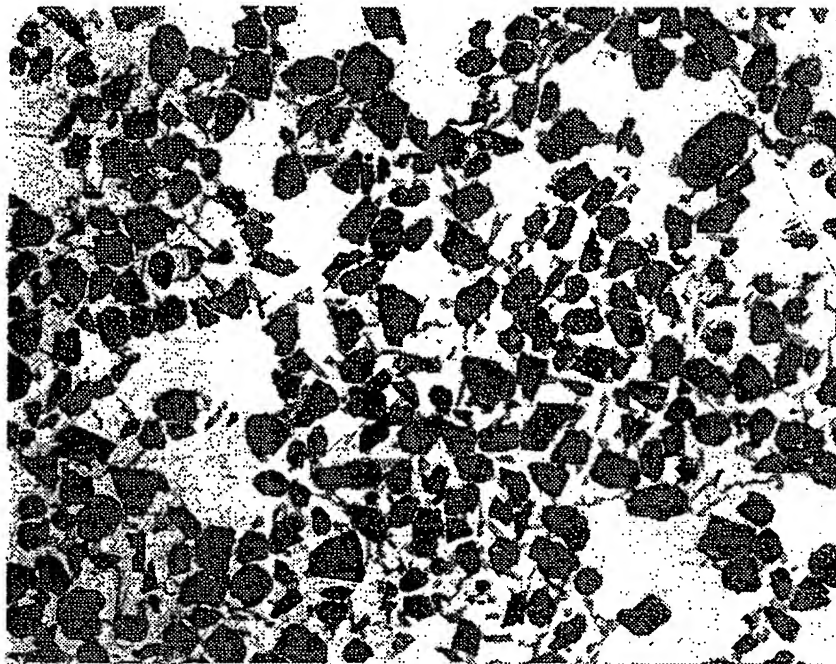


Fig. 23

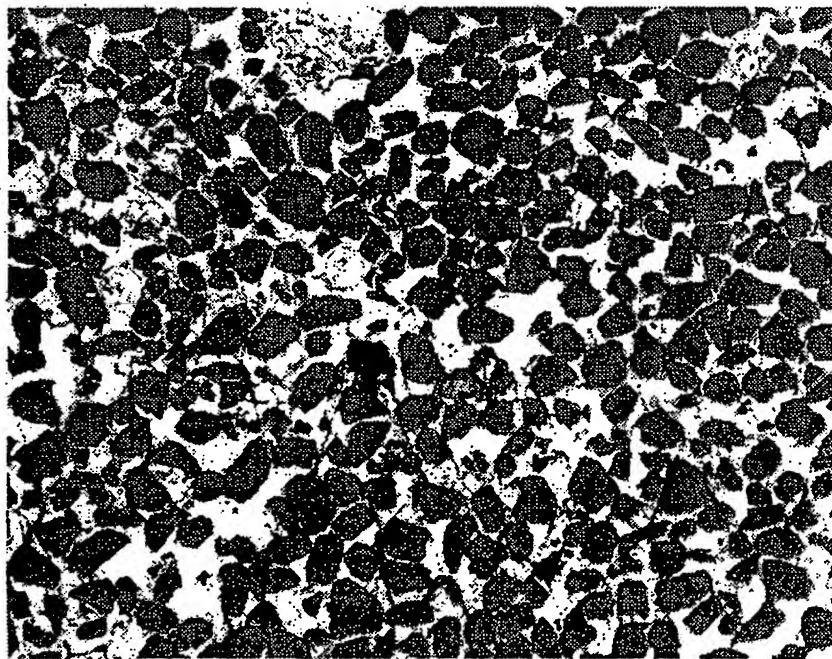


Fig. 24



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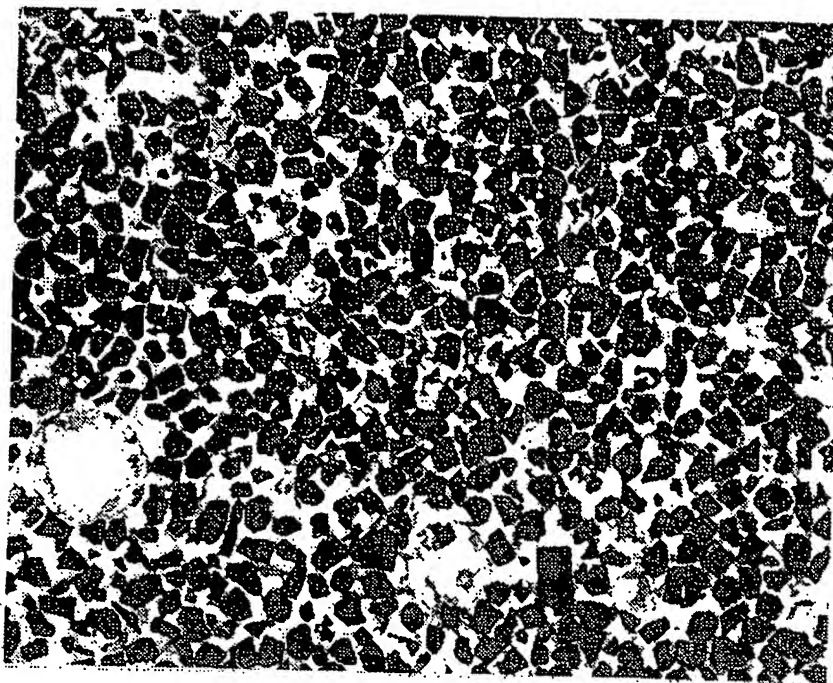


Fig. 25

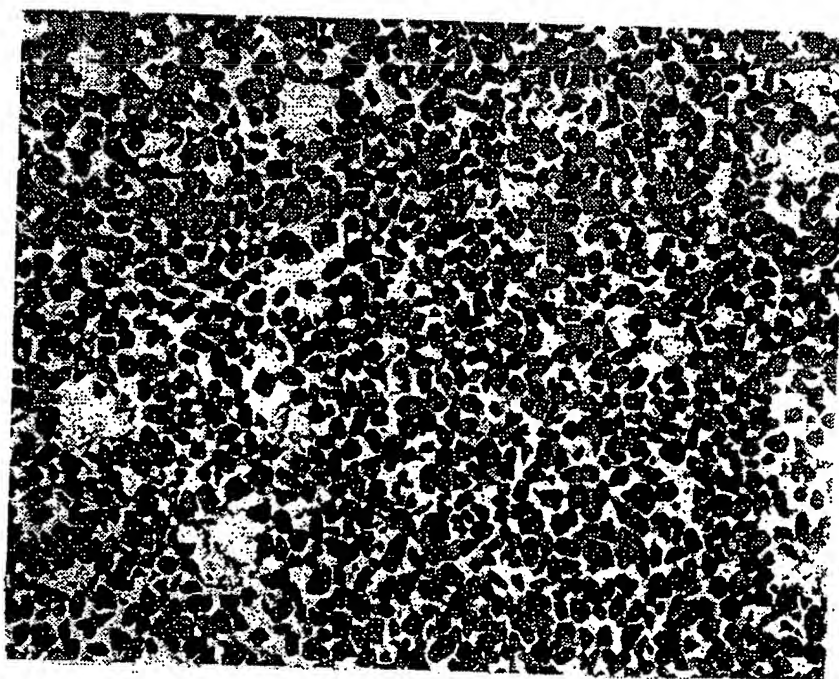


Fig. 26

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C22C1/10		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C22C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 482 (C-553) 15 December 1988 & JP,A,63 199 839 ( SUMITOMO ELECTRIC IND LTD ) 18 August 1988 see abstract	1-21
X	EP,A,0 375 588 (LANXIDE TECHNOLOGY COMPANY, LP) 27 June 1990 cited in the application see page 6, line 33 - page 7, line 18 see page 7, line 52 - page 8, line 1 see page 14, line 34 - page 15, line 20 see examples 5,7,12-15	1-21
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
10 MARCH 1993	23. 03.93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	RIBA VILANOVA M.	

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	<p>OPTICAL ENGINEERING vol. 27, no. 2, February 1988, BELLINGHAM, WA, USA pages 90 - 98 , XP5671 MOHN ET AL 'Recent applications of metal matrix composites in precision instruments and optical systems' see passage "2.2. Instrument-grade MMC materials" see figures 5-9</p> <p>-----</p>	1-21

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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9205927  
SA 62411

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10/03/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0375588	27-06-90	AU-A- 4384789	17-05-90
		CA-A- 2002284	10-05-90
		CN-A- 1045237	12-09-90
		JP-A- 2236244	19-09-90
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